

EMULSIONS AND FOAMS

By

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Preface

Emulsions and foams may be either desirable or undesirable. The progressive development of the art of producing and resolving them has been directed to their control. Formation, stabilization, inversion and transition to the unstable state are factors of importance in the study of emulsification and foaming. On the other hand, preventive measures in the formation of these systems as well as their destruction constitute major problems.

Emulsified oils have many uses in medicine (pharmaceutical emulsions), biology, food and vitamin chemistry, photography, agricultural spraying as well as in the petroleum, synthetic rubber, textile and leather industries. Asphalt, ~~bitumen and~~ lubricating-oil emulsions are discussed at length with specific ~~examples~~ of the broad application of hydrocarbon emulsions. Foams are desirable in such industries as brewing, wine, soap, ore flotation, and fire-extinguishing chemicals.

During the year 1940 the world's production of crude oil was over 2,200,000,000 barrels, of which the United States produced 1,350,000,000. Practically all crude oils produced contain salt water in a free state or in the form of emulsions. It is estimated that over 400,000,000 barrels of crude oil recovered yearly is in a highly emulsified state. Since pipeline transportation companies permit in general a maximum of 2 per cent of water emulsified in the oil, efficient demulsification must be effected in the field. The primary methods for breaking emulsions are by addition of chemicals, and by application of electricity, heat and pressure, or combinations thereof. Improved methods of oil production are reducing the amount of emulsification of crude oil.

Undesirable foaming and its prevention are problems related to heat dehydration of crude oils and tars, as well as to paper production and metallurgical practice.

It is believed that this book will provide a theoretical and practical background desirable in overcoming difficulties in oil foaming and emulsification. The methods of laboratory analyses outlined may also be useful.

We wish to acknowledge our deep indebtedness and gratitude to Dr. C. H. M. Roberts, Director of Research of the Petroleum Rectifying Company of California, for his valuable criticisms, contributions, and suggestions. Thanks are due Miss Eugenia Lieboner (M.Sc.) for typing the manuscript.

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Contents

CHAPTER 1. THE THEORY OF EMULSIONS AND FOAMS

Emulsions	<i>Page</i>
Introduction	1
Surface Tension	2
Viscosity	15
Solubility	23
Hydration	30
Volume Relation	34
Electric Charge	40
Size of Particles of the Disperse Phase and the Distribution of Sizes in an Emulsion System as Factors Relating to the Stability of Emulsions.....	53
Inversion of Phases in an Emulsion System and Factors Influencing It.....	60
Adsorption of the Emulsifying Agent at the Interface, Film Formation, and Variations in the Nature and Thickness of a Film as a Factor in the Stability of an Emulsion	71
Orientation of Molecules in the Adsorbed Interfacial Layer as an Explanation of Emulsion Stability and Other Emulsion Properties	90
Summary	101
1. Factors Influencing Emulsification	103
2. Factors Influencing Stability of Emulsion Systems	105
3. Factors Producing Inversion of Phases in Emulsion Systems	107
Bibliography	108
 Foams	
Introduction	112
Foam Formation	112
Origin and Mechanism	112
Formation of a single lamina	112
Forces acting in a lamina	114
Construction of a foam system	115
Conclusions	116
Factors Influencing Foam Formation	116
Vapor pressure and surface tension	116
Solubility and surface activity	119
Solubility, spreading, and viscosity	120
Boundary heterogeneity	122
Conclusions	127
Stability of Foam Systems	128
Factors in the Stabilization of Foam Systems	129
Influence of electrolytes	130
Action of protective colloids	131
Viscosity as a factor in the stabilization of foam systems	132
Action of finely divided solids	133
Forces Involved in Maintaining Stability	135
Electrostatic and capillary forces	135
Adsorption layer in the interface of a foam system and its thickness as a factor influencing stability; the Langmuir-Harkins orientation theory	136
Conclusions	140

	<i>Page</i>
Transition to the Unstable State	140
Forces Acting in the Thinning of a Film	140
Forces Influencing Transition to the Unstable State	142
Conclusions	146
Foam Prevention	147
Factors Influencing Foam Prevention	147
Summary	148
Bibliography	151

CHAPTER 2. PRACTICAL KNOWLEDGE OF EMULSIONS

Emulsification

Introduction	153
Methods of Preparing Emulsions	161
Emulsifiers	167
Electrolytes	171
Colloids	173
Resin Soaps	176
Water-soluble Gums	178
Organic Compounds	178
Sulfonic Acids and Sulfonated Oils	187
Sulfonated Products	188
Oils and Prepared Emulsions	196
Emulsification Processes	197
Types of Equipment Suitable for Use in Emulsification	199
Colloid Mills	199
Mixing Equipment	201
High-pressure Apparatus	203
Application of Centrifugal Force	204
Stirring Equipment	206
Appendix	211
Bibliography	212

CHAPTER 3. PRACTICAL KNOWLEDGE OF EMULSIONS

Demulsification

Introduction	219
Demulsification Methods	222
Heat Treatment	222
Methods and Equipment	234
Distillation	246
Indirect heat	249
Heat combined with mechanical treatment	253
Heat and pressure	264
Heat combined with centrifuging and filtration	268
Action of Chemicals and Demulsifying Agents	270
Demulsifiers	285
Acids, bases and salts	291
Solids	293
Gases	295
Colloids	297
Soaps	297
Alcohols	299
Hydroxy-derivatives	300
Condensation products	301
Organic acids and their salts	301

	<i>Page</i>
Sulfonated compounds	308
Blown oils	320
Distillation products (acid and alkali sludge, cracked residue, paraffin wax)	322
Freezing and Diluting	327
Desalting	328
Filtration	334
Electric Dehydration	338
Methods and equipment	344
Magnetic Dehydration	372
Centrifuging	373
Refining Processes and Methods for Preventing and Resolving Emulsions...	379
Bibliography	386

CHAPTER 4. PRACTICAL KNOWLEDGE OF EMULSIONS

Asphalt and Bitumen Emulsions

Introduction	396
Emulsification of Asphalt and Bitumen	405
Specific Methods for Stabilization of Asphalt Emulsions	421
Preparation of Bitumen Emulsions for Road Construction	426
Stability of Bitumen Emulsions used in Road Construction	429
Analyses of and Tests for Asphalt-Bitumen Emulsions	433
Methods employed in the Analysis of Asphalt Emulsions	434
Various Tests for Asphalt-bitumen Emulsions	435
Bibliography	441

Lubricants and Lubricating-Oil Emulsions

Introduction	445
Lubricating Power as a Function of Various Properties of a Lubricating Oil	447
Emulsibility and Viscosity	448
Capillarity	449
Adsorption and Wetting Ability	451
Oiliness	453
Various Tests for Lubricating Oils	454
Oiliness	454
Polarity and adhesion of the lubricant	455
Compressibility and tensile strength	456
Resistance to emulsification and sludge formation	457
Stability	458
Emulsification and demulsification	459
Methods for the Preparation of Lubricants and Lubricating-Oil Emulsions	461
Bibliography	465

CHAPTER 5. LABORATORY METHODS USED IN THE EXAMINATION OF EMULSIONS

Introduction	468
Sampling of Emulsions	468
Sampling Apparatus used in Well Gauging ..	470
Microscopic Examination	473
Test Methods	492
Surface Tension Measurements	494
Interfacial Tension Measurements	500
Spreading Tension Measurements	504

	<i>Page</i>
Wetting Tension Measurements	504
Viscosity Tests	507
Measurements of Electrical Properties	509
Emulsification and Demulsification	522
Investigation of the Emulsifier	525
Investigation of the Demulsifier	529
Stability	530
Determination of Emulsion Type	531
Determination of Emulsion Constituents	532
Salt and Acid	532
Oil	535
Water	537
Appendix	549
Origin of Petroleum	549
Physical Properties of Petroleum Indicating its Source	550
Oil Tests	553
Bibliography	561
Author Index	565
Subject Index	575

Chapter 1

The Theory of Emulsions and Foams

EMULSIONS

Introduction

The most typical and the simplest liquid/liquid dispersion system known is that of water in oil. It is evident that in such a system, known as an emulsion, the water globules are separated from one another, while the dispersion medium (oil) is the continuous phase. Oil globules may also be dispersed as droplets in water; the disperse phase in this case is oil and the dispersion medium, water. Both the dispersion medium and the disperse phase have a boundary surface; that of the former is concave, while that of the latter is convex. In the chemistry of dispersoids, the distinction between molecular and coarse systems depends upon the particle size of the phase distributed in the medium, that is, whether it is composed of molecules or aggregates of molecules, or of particles which can be readily seen under a microscope. The latter are called coarse systems. Between these two types of disperse systems (molecular and coarse) are the colloidal systems.

That petroleum and petroleum distillates may be of a colloidal nature has been indicated. It has been Ostwald's belief¹⁸³ that high-boiling petroleum fractions should be regarded as iso-colloids in which the disperse phase and the dispersion medium possess the same or similar chemical constituents. Pyhälä^{206,207} considers crude petroleum as a sol, the disperse phase of which is a solid gel, such as asphalt, together with liquid particles. Holde¹²⁴ states that mineral oils (petroleum and its distillates) are to be regarded as colloids. The heavy opaque mineral oils, which are considered as solutions of asphalt and lighter mineral resins in mineral oil, behave as colloids in a benzene solution. Reddish-yellow machine oils from paraffin oils were found by Dunstan and Thole⁶⁰ to contain amicrons and to display a blue cone of light. A small quantity of solid paraffin dissolved in benzene gives no cone of light, but larger quantities cause a cone of light and sub-microns to appear, and these increase in intensity with the concentration of the solution. Sub-microns are rarely found in Russian paraffin-free petroleum, but are readily detected in American paraffin-base oils. The fluorescence of petroleum has been attributed to its colloidal nature; but Brooks and Bacon⁸⁶ reported that this fluorescent material was not adsorbed by fuller's earth and that when it was diluted with kerosene, filtered and carefully dried, no such effect was noted in an ultramicroscope. Their contention was

that the fluorescence was due to the presence of a small percentage of aromatics, such as chrysene, pyrene and fluorene.

No demarcation can be made between the classes of dispersoids, as some intermediate transition systems are always present. But there is a twilight zone between coarse colloids and fine emulsions which cannot be defined according to observations, such as Brownian movement, cataphoresis, gel formation, and other phenomena occurring in emulsions. Generally speaking, it seems that it is the predominant size of the particles or globules of the disperse phase which determines the system to which an emulsion may belong. Emulsions, according to their properties, approach either coarse dispersions or colloidal systems. Many properties of emulsions which have number distribution curves with a maximum for small globules asymptotically approach those of colloidal systems, the stable state of emulsions being indicated, among other factors, by the presence of small globules. Gelatinization, so often observed in crude-oil emulsions, is a process of alteration caused by changes in emulsion concentration; it is also attributed to the presence of electrolytes or by-products in a colloidal state so well known in colloidal systems. The molecular portion of soaps in solution favors the rapid diffusion of a low molecular substance, whereas the colloidal portion causes gel formation. The division of natural emulsions into two groups of different properties, hydrophilic and hydrophobic, also supports the assumption that, even though characteristic differences exist between certain emulsions and colloids, they are systems of the same order. A great many investigators have studied the nature of emulsions, their properties, formation (emulsification), destruction (demulsification), and stability; but usually only a single system has been studied at a time, and that with respect to one or two significant factors or characteristics; no one system has been investigated in its many phases.

Many working hypotheses have been proposed, but only one or two of them seem to attain, even approximately, the value of a theory which might give a complete picture of and an explanation for emulsion behavior. Moreover, it must be noted that emulsions prepared artificially in a laboratory are not strictly analogous to those produced in oil wells. Nevertheless, a knowledge of the hypotheses offered by different investigators in the field of emulsions is of importance and practical value.

In the following chapters the most important factors which influence emulsion formation and affect their stability, as well as those which cause the inversion of emulsion systems, will be discussed.

Surface Tension

Surface tension has been emphasized as a factor in forming emulsions, as well as in maintaining their stability. Some workers in this field believe that surface tension is indispensable to the emulsification process and is the only significant factor in emulsion stability. Others do not deny a position of importance to this factor, but point out many cases of emulsion formation in which surface tension does not play as great a

part as other characteristics of the system. In some cases surface tension can be shown to have little, if any, part in the formation and stabilization of emulsions.

Surface tension in an emulsion system refers to the surface tension of a liquid/liquid boundary surface and is called interfacial tension. The interfacial tension of a liquid/gas boundary is significant in the case of oil-well emulsions when gas is present and under conditions favoring creaming and foaming. The adsorption of substances at the boundary surface is important in effecting a change in the surface tension of a system brought about by the addition of a substance, or by the presence of by-products in the system. The surface tension of a freshly formed surface of a soap solution differs little from that of water, but decreases rapidly as the soap molecules become adsorbed at the surface. Molecules of a solute which reduce the surface tension become more concentrated at the boundary surface than in the interior of the solution. This type of adsorption is called positive. When negative adsorption takes place, an increase in surface tension occurs in the system. A decrease in surface tension is more frequent than an increase. It is readily understood that stabilization may be due to either positive or a negative adsorption,^{74a} involving a difference in composition between the surface layer and the volume, and that emulsification is brought about only by substances which lower the surface or interfacial tension, it being known that interfacial adsorption is merely a lowering of the interfacial tension. When the concentration of the solute of the emulsifier is sufficiently high, it may lead to the formation of an invisible skin or tough membrane. The formation of adsorbed films in the interface is considered an important factor in the stabilization of an emulsion, because it prevents the coalescence of its globules. Coalescence is facilitated by the Brownian movement of the droplets. Brownian movement causes the droplets to diffuse slowly through the liquid and to collide with one another repeatedly. This sudden decrease in interface produces a momentary increase in the thickness of the adsorption layer and therefore a decrease in the interfacial tension, provided the surface layer is not saturated. But even when the interfacial tension is reduced to zero, some tendency to coalesce still remains.

According to thermodynamics, it is readily understood that low interfacial tension favors emulsification. When two immiscible liquids are agitated so as to disperse one liquid in the other in the form of fine globules, the surface of each liquid becomes greatly extended, and a correspondingly large quantity of free energy is produced at the interface. The work of extension (or the potential energy appearing at the interface, as well as at the free surface) is measured by the area of the surface produced and the intensity of the interfacial tension acting against it. Gibbs says that the free energy possessed by a surface "is at once the spring of its activity and the seed of its destruction." It is obvious that this potential energy of the surface, just as the potential energy of any other system, tends to reduce the area of the surface to a minimum. This

contractile force draws the liquid into a number of spherical droplets, and at the same time divides an intimate mixture of two immiscible liquids into two phases, separated by the smallest possible interface. Therefore, if an emulsifying agent reduces the interfacial tension between two immiscible liquids, it decreases the free surface energy of the emulsion formed and tends to produce a permanent emulsion. At the interface and between the phases of an emulsion, two antagonistic forces are at work, namely, surface tension, which tends to cause coalescence, and coherence of the film of emulsifying agent, which tends to resist coalescence. Therefore, the stability of an emulsion is dependent on the relative magnitudes of these opposing forces. If the coherence of an emulsifying agent is so great that surface tension cannot overcome it, the emulsion becomes "permanent." If this is true, then a general method should be available whereby the stability of an emulsion may be decreased, namely, by an attack upon the emulsifying agent resulting in an increase in the interfacial tension. To convert the emulsifying agent into an ineffective form, a substance should be added which dissolves and removes it from the interface, causes it to flocculate to such an extent that a coherent film is no longer present, or tends to form the reverse type of an emulsion, *e.g.*, a counter-colloid.

In many emulsions a marked lowering of the surface tension may be attributed to the emulsifying agent, and it can be increased only by destroying or modifying the latter. It is the contention of Bancroft^{9,10,11} that emulsification is due largely to the small surface tension between the oil and the emulsifying agent, which permits the latter to spread out in a thin film separating the oil globules. When two liquids come into contact at a common interface, a mutual pull is exerted, with a resulting reduction in surface tension; and this pull tends to cause one liquid to spread over the other. The stronger the force of adhesion between the molecules of the two liquids, the smaller the interfacial tension and the greater the degree of spreading. If the force of adhesion is as great as or greater than the force of cohesion of the spreading liquid, the liquid will spread until it forms a continuous monomolecular film. If a liquid which is in a position to spread over another liquid, possesses a force of cohesion greater than its force of adhesion to water, it will not spread. If adhesion is stronger than cohesion, it will spread to an extent determined by the spreading coefficient S , which is equal to the difference between the work of adhesion W_a , required to separate the liquid from the water, and the work of cohesion W_c .

Harkins^{100,101} showed that the force of adhesion between various fatty acids and water is practically the same in every case, no matter how long the carbon chain may be. From this he concluded that in every case the force of adhesion represents the attraction between carboxyl groups and water molecules. The work of adhesion depends upon the strong active groups in the molecule, and the work of cohesion upon both weak and strong polar groups.

An experimental method to show that surface tension of the emulsify-

ing film is higher on the side of the emulsified liquid was devised by Bancroft and Tucker,¹⁵ who applied the theory of Gibbs, which assumes that a film has two surfaces and two surface tensions when it is in contact with different phases. These two surface tensions are not necessarily equal, and the film will tend to curl toward the side having the higher surface tension. In all emulsions the dispersed liquid is on the side of the film having the higher surface tension. The low interfacial tension between two liquids, as usually measured, is the difference between the surface tensions on the two sides of the film. For example, oleic acid may be drawn into globules on a surface of water previously wetted by the acid because the surface tension between the adsorbed oleic acid and the oleic acid in a body is not zero. It is the belief of Bancroft and Tucker that there is no method of predicting the type of emulsion by any other property than the surface tension of the film, although the liquid that wets the emulsifying agent more readily is usually the dispersing medium.

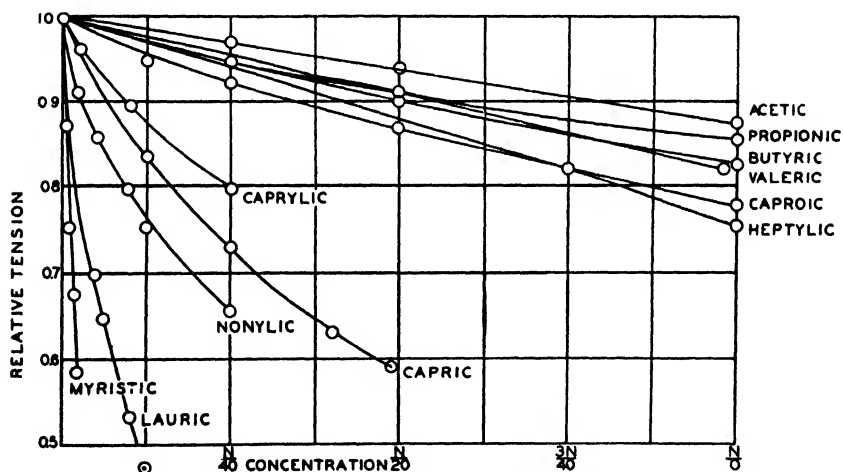


FIG. 1. Organic Acids Reducing Interfacial Tension.

The first to relate lowering of surface tension with emulsification were Quincke^{208, 209} and Plateau,^{199, 200} who showed that good emulsifying agents generally form solutions having low surface tension. A series of experiments, which showed a striking correlation between the emulsifying power of the sodium salts of monobasic fatty acids for a petroleum lubricating oil and the reduction in surface tension which they produced, was carried out by Donnan and Potts.⁵⁹ These investigators measured the relative interfacial tension between a hydrocarbon oil and the aqueous solutions of a number of sodium salts of normal saturated fatty acids at various concentrations and found that all salts decrease the interfacial tension; sodium caprylate is the first to show a marked effect in lowering the interfacial tension, the effect increasing rapidly with increase in

molecular weight (Fig. 1). In measuring the emulsification with hydrocarbon oils of aqueous solutions of salts of fatty acids of various concentrations, they found that the sodium salts of lauric and myristic acids had a measurable emulsifying ability. In these cases the emulsification first increases rapidly at low concentrations and then decreases rapidly at high concentrations. It has been stated by Donnan and Potts that the maximum concentration necessary for emulsification can be partially accounted for by calling attention to the "salting out" or coagulating action of the positive sodium ions. Gurwitsch^{91,92} found that the correlation of the lowering of surface tension and emulsion formation is applicable to petroleum emulsions also, and showed that resinous substances and naphthenic acids, which are efficient agents for promoting emulsification of petroleum oils, greatly reduce the surface tension of these oils when the latter are in contact with water, as shown in Table 1.

Table 1.

	Surface Tension Against Water (ergs/cm ²)
Liquid paraffin	47.2
Liquid paraffin + 1% naphthene soap	30.5
Liquid paraffin + 3% petroleum resins	40.1

Harkins, Brown and Davies^{105a} found that sodium oleate (0.03*N*), which is an excellent emulsifying agent, reduced the surface tension of water against water vapor from 72.8 to 26.75 dynes/cm. At the same time, it reduced the interfacial tension between water and benzene from 35.0 to 2.22 ergs. Moreover, Harkins and Zollman¹⁰⁹ found that if, instead of using a previously prepared sodium oleate solution, a proper amount of sodium hydroxide with some sodium chloride were added to the aqueous phase and the benzene phase contained an equivalent concentration of oleic acid, the interfacial tension could be reduced to 0.04 erg/sq. cm, that is, about one-thousandth of its original value.

It was observed by Reinders²¹⁰ that powdered metals and insoluble salts in water, when shaken with ether, kerosene, alcohols, etc., are adsorbed in the interface. According to Quincke, if three liquid phases in equilibrium with one another are brought together, then, depending upon the values of the interfacial tension, $\sigma_{1,2}$, $\sigma_{2,3}$, and $\sigma_{3,1}$, either the three phases meet at a mutual edge, or one of the phases spreads out between the other two, separating them wholly. From the standpoint of the force of gravity, the first takes place when either one of the two interfacial tensions is greater than the sum of the other two, and the second condition implies that this is actually the case. For example, if $\sigma_{1,2} > \sigma_{2,3} + \sigma_{3,1}$, then phase three will spread out between the first and second phases.

When a colloid is a suspensoid and the solid particles contained in it have dimensions for which a constant surface tension with respect to the surrounding phase may be assumed, three possibilities may be mentioned: (1) the colloidal substance remains in the first dispersion agent; (2) the

colloidal substance reaches the boundary; or (3) the colloidal substance passes completely into the second liquid. If the particles of the dispersed phase are so small that they may be considered as aggregates of relatively few molecules, then the surface tension of these aggregates is greatly dependent on the number of these molecules; and it may happen that colloidal solutions of one and the same substance show an unlike behavior with respect to a second liquid, depending upon the size of the particles. When the particles reach molecular dimension, the dissolved substance intermingles with the two solvents according to the Law of Distribution, factors other than surface tension being responsible.

Reinders,²¹⁹ experimenting with powders of various kinds of insoluble inorganic compounds shaken with water and an organic liquid, found that in a few cases the powder went completely into the aqueous phase; in others, the organic liquid contained practically all the suspension, but in the great majority the solid went preferentially or completely to the interface. If it is to be concluded from this that the interfacial tension involved is diminished by the addition of most inorganic solids, it is not logical to deduce that the tension at each of the solid/liquid surfaces should also be considered, because the particles are comparatively large. (The solid will go to the interface if each liquid is adsorbed at the surface between the solid and the second liquid, that is to say, if the mutual solubility is increased at the surface of the solid.)

The cleansing power of soap was attributed by Smith²⁵¹ to the fact that soap solutions have a low surface tension compared with that of pure water, but approximately of the same order as that of many oils. When two liquids having about the same surface tension are mixed they do not separate, because the tendency to form larger droplets is not greater in one case than in the other. The separation of oil and water is brought about largely by the high surface tension of water. The droplets of water combine to form larger droplets with greater force than do the droplets of oil, that is, they come together with such force that the oil is pushed away and freed, forming a separate layer.

The surface tension of pure sodium palmitate and sodium stearate solutions of various concentrations was measured by White and Marden,²⁸¹ who found that the surface tension increases with increase in concentration. This is contrary to the change in surface tension shown by alkali and salt solutions. The relative emulsifying power of solutions of sodium palmitate and sodium stearate with kerosene and linseed oil was determined by shaking them by hand for five minutes and observing the time for noticeable separation. The relationship between the surface tension and emulsifying power of the solutions studied was such that, with an increase in concentration of the soap solution, there was an increase in the emulsifying power; or vice versa, as the surface tension increased, the emulsifying power decreased. The presence of glycerin does not affect the surface tension of a soap solution to any great extent; therefore it should not have an injurious effect on the cleansing power of soap. A large percentage of sodium carbonate, however, was found to increase the

surface tension, and for this reason would not be desirable in soaps, according to these investigators.

In order to answer the question regarding surface tension of soap solutions, Lascaray¹⁴⁷ made measurements at ordinary temperatures, using Traube's stalagmometer, and found that the surface tension of soap solutions changes gradually, going from inactive sodium formate up to the strongly active higher members of the series.

The surface tension curve of the middle fatty acid salts (sodium caproate to sodium laurate) shows a break which coincides with the sudden clearing of the solutions. Lascaray¹⁴⁷ found an interesting phenomenon for the coagulation processes involved. He differentiated two kinds of coagulation, namely (1) the dilute soap solutions which, when fresh, have a strong turbidity and form by coagulation a precipitate (coagulum) which is lighter than water and which therefore rises to the top; on the surface of the solution a layer is formed which is liquid for sodium caproate, sodium caprylate and sodium oleate, but solid for sodium laurate; coagulation proceeds comparatively slowly. (2) The sudden rise of the surface tension curve which coincides with the sudden clearing is accompanied by a change in the coagulation process; the solutions, which suddenly become almost clear, do not give a coagulum (precipitate) which is lighter than water but, on the contrary, a heavy flocculant precipitate which accumulates at the bottom of the container. When coagulation is completed (and that quickly), these solutions are totally clear.

Lascaray attributes the difference in precipitation to the fact that they originate from two sols, and assumes that their formation indicates the presence in soap solutions of fatty acid, as well as soap sols which, after coagulation, are converted into fatty acids and solid soaps. Both colloidal systems may be present in a soap solution at the same time. For the existence of a fatty acid sol, it is necessary that the amount of fatty acid present be greater than that molecularly dissolved in water, and this amount depends on hydrolysis. The concentration of the fatty acid set free by hydrolysis for the same substance depends only on the concentration of the ions present and is proportional to the square root of this concentration. The electrochemical laws of solutions show that the ion concentration of a salt reaches a maximum with increase in the concentration of the salt, and then falls again. The same holds true for the concentration of a hydrolyzed fatty acid. In relatively dilute solutions, hydrolysis may be extensive, and the amount of hydrolytically split fatty acids may be greater than that which will go into solution. Soap solutions are good dispersion agents; therefore a fatty acid sol is formed. In the case of concentrated solutions, hydrolysis is insignificant, and the amount of hydrolytically split fatty acids is small, molecularly dispersed solutions and no fatty acid sols being formed. Soap solutions, on the other hand, originate principally in concentrated solutions because they are formed directly from soap molecules.

Heyden von Typke¹¹⁹ states that the surface tension of cutting oils, used in the preparation of white emulsifying oils and possessing good pro-

tective properties against rust, is affected by the presence of soap. In commercial practice, homogeneous cutting oils are obtained by using an aqueous alcoholic base or an excess of free oleic acid for saponification. In the emulsification of cutting oil in water, the emulsion is made more complete and more stable the smaller the surface tension between the soap solution of the cutting oil and the mineral oil. When no surface tension is present, cutting oils are obtained which are actually water-soluble and not just emulsified by water.

The surface tension of emulsions is affected by the presence of electrolytes in various concentrations. Limburg¹⁵⁶ investigated the influence of electrolytes on the interfacial tension of a system of paraffin oil and water, and found that the interfacial tension of oil-in-water emulsions did not change greatly with the use of various concentrations of hydrochloric acid or potassium chloride, but decreased rapidly for increased concentrations of potassium carbonate. Limburg found that the stability of emulsions decreased with increase in the concentration of most salts, and that the relationship between stability and charge did not indicate either the proportionality or the existence of a critical potential. However, at low concentrations of electrolyte, for example, hydrochloric acid, the charge was increased but, in spite of this, the stability decreased. From this, Limburg deduced that the increase in conductivity is the important factor determining stability. With an increase in concentration of electrolyte this effect becomes so great that, in spite of the protective action of the charge, the coagulation velocity reaches its highest value and the charge becomes ineffective. Thus decrease in stability with increase in the concentration of electrolyte (regardless of two favorable factors, *i.e.*, charge and surface tension) is ascribed by Limburg to an increase in the conductivity of the solution. This fact he considers as contradicting both the critical potential theory of Powis and the conception that the stability of an emulsion is determined solely by the value (magnitude) of the charge.

The surface tension of oil-in-water emulsions was observed by Joshi.¹³³ The system investigated consisted of pure water, oil, and a solution of sodium oleate. The surface tension was found to be practically identical with that of the dispersion medium in a pure state and not dependent upon the nature of the dispersed phase. Oil, dirt, or other impurities diminish the surface tension when they are present as such, and not emulsified in the system. If they are emulsified in the liquid they can be present in a larger proportion without having any influence on the surface tension.

Russakow, Kuznetzowa and Ssemenko,²²⁹ working with pure paraffin oils and commercial oils, considered surface activity an important factor. By measuring the surface tension of commercial oils against water and air they established the fact that the change in the interfacial tension, when oils were treated with refining agents of various concentrations, is parallel with the stability of the oils investigated. Further, these investigators were of the opinion that measurements of surface tension against

dilute alkali solutions may determine the percentage of oil in the saponifiable substances. Holmes and Williams¹²⁸ state that not every substance causing a marked lowering of interfacial tension will act as a good emulsifying agent. For instance, acetone is soluble in benzene and water and lowers the surface tension, yet shows no emulsifying power; and the same is true of methylethyl ketone.

There are many cases of emulsion formation in which surface tension is apparently of slight importance. A number of investigators have prepared stable emulsions by using finely divided solids, which are insoluble in either phase, and do not affect their surface tension. Carbon black was found by Schlaepfer^{233, 234} and Moore¹⁷⁴ to be an excellent emulsifier in the formation of water-in-kerosene emulsions. Very stable emulsions of kerosene and solar distillate in water were prepared by Pickering,¹⁹² using finely divided solids as emulsifiers. Particularly effective as such were the basic sulfates of iron, copper, nickel, zinc and aluminum, which may be due to the formation of a salt with the oil. In many cases, the surface tension of the dispersing medium no doubt plays an important role in emulsification; then again, where emulsification is due to the presence of solid particles, no changes in the surface tension of the dispersing medium takes place. On the other hand, some investigators believe that even in emulsification by pulverized solids, lowering of surface tension is involved.

It has been stated by Hatschek¹¹⁵ that substances used by Pickering obviously would not accumulate at the interface, particularly on the water side, unless this arrangement led to a lowering of the interfacial tension. Liesegang¹⁵⁵ contends that the collection of fine particles at the surface of the water phase brings about a reduction in the surface tension.

Table 2

	Specific Gravity	Surface Tension (dynes/cm)		Specific Gravity	Surface Tension (dynes/cm)
Isohexane	0.664	22.5	* Miner's Oil	0.874	33.7
	0.800	29.6	* Diamond Paraffin		
	0.818	30.2	Oil	0.887	34.4
	0.834	31.7	* 2900 Red Oil	0.895	35.0
	0.852	32.8		(b.p. over 270°)	
			Casein (0.02%)		54.8
			Water		74.2

* Oils obtained from a series of 35 petroleum distillates.

In a series of emulsions prepared with oils of increasing specific gravities dispersed in an aqueous solution of casein, Seifriz²³⁵ found no relation between the surface tension of the oils or of the casein solution and the formation of either oil-in-water or water-in-oil emulsions, as shown in Table 2.

These data reveal no apparent relationship between the surface-tension values of oil and the type of emulsion formed. However, there is a uniform increase in the surface-tension values at the rate of about one

dyne for every 0.02 increase in specific gravity, yet the surface-tension values for all the oils were far below that of aqueous casein.

The investigations of Meunier and Maury¹⁶⁸ indicate that fatty acids have an emulsifying action greatly superior to that of neutral fats and that, in the case of mixtures of free fatty acids and neutral fats, the stable emulsions which can be formed are due mainly to the former. They showed also that if an alkaline solution is substituted for water as the dispersion medium, the surface tension of contact is still further decreased. These investigators are of the opinion that every solid or liquid substance capable of being precipitated or emulsified in the form of fine particles may act as an emulsifying agent, especially if its interfacial tension against the dispersion liquid is inferior to that of the oil to be emulsified.

Some attempts have been made to draw a relationship between changes in surface tension and other characteristics of the emulsion system influencing emulsification, including stability. Sheppard and Sweet²⁴³ endeavored to establish a relationship between the stability of emulsions and the surface tension of a saturated toluene solution of gelatin, taking into consideration the H^+ ion concentration of the emulsifying agent, but the results obtained were not satisfactory; in very strong acid or alkali solutions, the curves of stability did not follow the curves of the surface tension. The experiments of Nugent^{181, 182} proved that gelatin, when used as an emulsifying agent in oil-in-water emulsions, forms a film around the oil globules. This fact led Zhukov and Buschmakina²⁹⁰ to investigate the surface tension of a benzene-in-gelatin solution; they obtained a sharply pronounced minimum of surface tension when the pH of the gelatin solution, determined potentiometrically, was 5.27 (pH = 5.25 corresponds to the iso-electric point). Moreover, they assumed that the minimum surface tension at the iso-electric point is the condition under which gelatin contains neither hydrated nor dissociated particles, and the neutral molecules are packed close together on the surface of the benzene globules, showing maximum adsorption power. It is the opinion of Hartridge and Peters^{111, 112} that the surface tension developed at the interface between oil and water varies with the pH of water. When the pH is low, indicating an acid condition, the surface tension is high, and vice versa. Near the neutral point, using olive oil and 1/1000N sodium hydroxide, they found a drop in surface tension of about 35 per cent for a change of pH equal to one. For paraffin and water, no such decrease was observed, and for benzene the decrease varied and was negligible.

Pound^{201, 202} states that the interfacial tension of pure liquids in water is constant at a definite temperature, and that the interfacial tension between two liquids is less, the greater their mutual solubility. The interfacial tension of oils in contact with water usually varies with the age of the interface and frequently decreases with time. In these cases the interfacial tension is less than the difference in the surface tension of the mutually saturated liquids. Such a decrease in interfacial tension with time is probable, for example, with paraffinic oils and water. Fur-

ther, when a chemical change takes place at the interface, the interfacial tension changes; in particular, soaps of fatty acids undergo hydrolysis when in contact with water, and the resulting changes at the interface help to lower the interfacial tension. The rate of lowering of the interfacial tension becomes slower as the interface grows older.

Measurements made by Nasini, Rossi and Santa¹⁷⁸ on the interfacial tension between mixtures of organic liquids and emulsifiers, such as benzene/amyl acetate, toluene/amyl acetate, benzene/toluene, nitrobenzene/carbon tetrachloride and benzene/liquid petrolatum, in the presence of sodium lauryl sulfate and water, indicate that the decrease in surface tension is in accordance with the findings of Mathews and Stamm.¹⁶² These investigators give data for the interfacial tension of dimethyl aniline-heptane in water and dimethyl aniline-benzene in water, which indicate that up to concentrations where, because of polarity, a complete surface layer is formed, the interfacial layer is one molecule thick; thereafter the thickness begins to increase.

A parallel between surface tension and wetting ability was found by Nellensteyn¹⁷⁹ for asphalt and tar. This investigator discusses the wetting ability of liquids in relation to capillary phenomena. A low surface tension enables a liquid to spread over a smooth surface, but does not favor its rise in a capillary tube. The surface tension of various mineral oils, asphalts, and coal tars was determined at 180-200° by noting the differential rise in wide and in narrow capillary tubes. In an atmosphere of nitrogen, the surface tension of mineral asphalts varied between 23 and 25 dynes/cm; for coal tar, the values were found to be 43.0, 46.9, and 32.0 dynes/cm at 20°, 50°, and 190°, respectively.

It has been pointed out by Gand and Neal^{82,83} that olive oil in small amounts decreases the surface tension of acidified water and that large amounts increase it. Most oils do not alter the surface tension of water and alkali. From this they concluded that the chief significance of flotation is not due to the action of oil upon the surface tension. It is apparent that the foaming ability of the oil, and not its surface tension, is of importance.

A number of investigators drew a relationship between the stability of an emulsion system and a change in surface tension. Groschuff⁸⁹ reported on the stability of oil-in-water emulsions and claimed that neither the density of the oil nor the solubility of the water in the oil gives any idea of the stability of emulsions, for stability of emulsions at equal temperatures is a function of the surface tension, that is, the stability increases when the interfacial tension between phases decreases. As stated by Roberts, this is not necessarily true. Tretolite lowers interfacial tension and breaks emulsions. California emulsions have 0-10 dynes interfacial tension; Mid-Continent emulsions have 10-25 dynes, and the latter are more stable than the former.

The addition of mineral salts, alkalies, and acids promotes the formation of emulsions because these decrease the surface tension between oil and water. The action of colloids and impurities on emulsification

is considered to be analogous. Bechhold and Silbereisen¹⁷ conducted a series of experiments on surface tension, the results of which are given in Table 3.

Table 3

Emulsion	Surface Tension	
	(dynes/cm)	Temp. (°C.)
Glycerin/isobutyl alcohol	0.038	19
Isobutyl alcohol/water	1.73	19
1% Aqueous solution of sodium lysalbinat	1.715	
Sodium protalbinat	1.535	

The glycerin/isobutyl alcohol system, which has a minimum surface tension, is demulsified three times more quickly than the isobutyl alcohol/water system, with sodium lysalbinat as the emulsifier, the surface tension of which is forty times greater. The fact that demulsification of the glycerin/isobutyl alcohol emulsion does not take place at a greater rate was accounted for by the high viscosity of the glycerin. When one per cent of sodium lysalbinat or sodium protalbinat was added to the isobutyl alcohol/water system, the time of demulsification, *i.e.*, changes in stability, was found to increase from one minute to one to three hours, or 60 to 180 times, although the surface tension decreased only to a minimum extent, namely, from 1.73 to 1.715, or 1.535 dynes/cm. These investigators conclude, therefore, that low surface tension does not always influence the stability of emulsions.

In a study of pharmaceutical emulsions, Marshall¹⁸¹ found no explanation for emulsification other than the fact that it is a phenomenon of surface tension. This investigator assumed that, when a sphere is subjected to negative surface tension, the system is evidently unstable, since the molecules move in the direction of greatest attraction; the sphere disintegrates when it is surrounded by a liquid the molecules of which exert a greater attraction on the molecules of the liquid sphere than on one another. This factor is important in demulsification.

From experimental evidence of several investigators, it has been concluded that it is not the surface tension alone that influences the formation and stabilization of an emulsion, but that changes in the electric charge of the dispersed phase also have their effect. According to Lerch,¹⁴⁸ surface tension at the interface of two solvents is influenced by the distribution of an electrolyte, and this influence is partly of an electrical nature. In the neutralization of an acid by a base, a point is reached at which a very small addition in one direction or another produces a change in surface tension (surface tension of distilled water is 72.5; 0.5*N* hydrochloric acid, 72.3; 0.5*N* sodium hydroxide, 74.4). Kendrick¹³⁴ assumed that there is a parallel between the action of certain substances upon the surface tension and the potential drop at the boundary surface of water and oil. Changes in surface tension are related to changes in electrical potential and, in all probability, selective ion adsorption also plays a part. Kendrick's viewpoint was disproved by Harkins.¹⁰³

McLewis¹⁵² calls the two chief factors in the equilibrium of an emul-

sion particle (1) the surface tension, and (2) the electric charge. The concepts presented in "Modern Views of Electricity" by Sir Oliver Lodge also lead in this direction, namely, that the concentration of moisture on a charged nucleus is similar to the relation between surface tension and electric charge, and can be applied to the equilibrium of an emulsion particle. The rapid evaporation of a small globule is based on the curvature of its surface and on its surface tension. An electric charge tends to diminish this, apparently producing a small surface pressure. A charged soap bubble is slightly larger than an uncharged one. The actions of the surface tension and the electric charge are opposed to each other, one being tangential and the other radial in direction. Tangential tension results in a convex surface, and is directed toward the inside of a liquid globule, whereas radial tension is directed toward the outside of a liquid globule.

Surface tension which is due to the cohesion of surface molecules in a liquid is an important factor, particularly for small globules, even if the circumference is of moderate magnitude. The repulsion obtained through a given electric charge is usually small, increasing rapidly as the charged body becomes smaller; the action of cohesion changes inversely with the diameter of the globule, and the action of the electric charge changes inversely as the fourth power of the diameter of the globule. Therefore, when the globule becomes smaller, both opposing tendencies necessarily equalize each other and the action of its curvature is removed; thus the globule behaves as if it were a plane. Such a globule can exist as readily as any liquid having a plane surface, and each globule will become smaller the greater the force of cohesion, finally reaching a state of equilibrium.^{3a}

By equating the capillary and electric pressures of the surface of an emulsion particle, Lewis found the following equation to be true:

$$\tau = \frac{\sqrt{e^2}}{16\pi\sigma K}$$

He also states that if this equation is correct, the surface tension, σ , of such particles is only a small fraction of the tension which exists where the phases are separated by a plane boundary surface.

In this manner, the literature on emulsions describes emulsification and conditions of stability as a function of surface-tension changes alone, or in connection with other factors, such as electric charge, solubility, wettability, etc. It cannot be claimed that a complete picture or a full explanation of the behavior of emulsion systems considered has been presented. The results obtained by one investigator or another for one emulsion system cannot be extended to other emulsion systems distinguished by the varying nature of substances building up the single phases of the system. Every emulsion system must be treated according to various methods in order to obtain a few characteristics for that system.

Viscosity

The viscosity factor must be taken into consideration in three cases, namely, (1) when the emulsion is prepared from a viscous oil, such as Stanolax (heavy paraffin oil) and water; (2) when the emulsion system is viscous because of the presence of by-products, or of the addition of an emulsifier; and (3) when the previously prepared emulsion becomes viscous on ageing, or as a result of other changes occurring in the system, such as variations in temperature, etc.

Viscosity exerts a greater influence on the stabilization of emulsions than on emulsification itself. In the case of emulsions, one is concerned with the internal type of viscosity, or the internal friction. If viscosity is considered as giving permanence to oil globules, it is referred to as "interfacial" viscosity, which makes movement between globules difficult and prevents coalescence by decreasing the rate of thinning of the film between the globules. Viscosity alone in an oil-in-water emulsion prepared from a viscous oil does not appear to be an important factor in rendering an emulsion system stable. Experiments have shown that octane/water emulsions are sometimes more stable than Stanolax/water emulsions. Pure liquids, true solutions and colloids are employed in the preparation of emulsions. There is a great difference between the viscosity of a pure liquid or a true solution and that of emulsoids, such as solutions of gelatin or gum arabic, which are often used as emulsifying agents. Bancroft,^{9,10} discussing the question whether emulsification can be explained by the viscosity of the emulsifying agent, stated that in the case of very viscous liquids (gum solutions) it is probable that high viscosity may be a deciding factor in giving permanence to oil globules mechanically formed. Canals and Mousseron⁴² showed that the emulsifying ability of gum arabic and tragacanth for emulsions of olive oil and sweet almond oil in water varies with the viscosity of the system. Taking the viscosity of water as a unit, tragacanth was found to be more efficient than gum arabic when the viscosities were high (16.0 and 15.4, respectively); but at low viscosities (7.1 and 9.2, respectively) gum arabic was much more efficient than tragacanth. From this, these investigators concluded that "it is quite probable that the two gums stabilize emulsions in different ways."

That even very high internal viscosity will not make an emulsion permanent in some cases has been shown by Hillyer¹²¹ for such viscous solutions as 50 per cent glycerin and 6 per cent gum, which would not emulsify kerosene, or even so viscous an oil as cottonseed. Then again, viscosity may have very little to do with the emulsifying power, as for example, in the case of dilute soap solutions containing about one per cent of sodium oleate. It is a fact that soaps are excellent emulsifying agents; but they may have such low viscosity that accurate measurements are necessary to prove them more viscous than water. Thus, internal viscosity of a liquid does not always account for its emulsifying power.

Saponin or albumin solutions have a high surface viscosity. This type of viscosity hinders the withdrawal of films of saponin from between

oil droplets in a saponin-oil emulsion, and consequently is responsible for the permanence of the emulsion. A high internal viscosity or high surface viscosity may play a role in retarding the thinning of the interfacial film and thereby assist in maintaining the emulsion.

Höber¹²² states that the emulsifying agent itself must be a colloid, and considers a stable emulsion analogous to a colloidal suspension which has been rendered stable by means of a protective colloid. Freundlich⁷⁶ is of the opinion that colloidal substances, such as soaps, glue, starch and albumin, are especially effective as emulsifying agents because they diffuse slowly and their adsorption and equalization of differences in concentration does not take place rapidly; therefore differences in surface tension remain long enough to allow mechanical action to take place.

In Beck's experiments¹⁸ on the viscosity of suspensions of oil in water in the presence of emulsifiers, it was found that the viscosity of a liquid is essentially increased only when the suspended particles are present in such an amount that they are brought into contact with one another, as is the case in sludge formation. It is interesting to note that fine suspensions, as obtained in colloidal solutions, influence the constant of internal viscosity, or friction, of the suspension medium. This can be explained by the fact that the suspended particles collide with one another at distances of molecular dimension.

Of interest has been the question whether, starting with a definite concentration of a suspended oil analogous to sludge formation or colloiddally dissolved substances, there is an increased influence on the viscosity. The first experiments with a cholesterol-in-water emulsion gave no tangible results; therefore a castor oil-in-water emulsion containing gum arabic was substituted. A correction factor was introduced into this experiment because gum arabic itself increases the internal friction. The results obtained by Beck indicate that a suspension of oil in water up to 10 per cent of oil has no essential influence on the constant of internal friction. Higher concentrations of oil cannot be used because of separation into its respective components. In the presence of gum arabic as the emulsifying agent, the viscosities of the emulsions showed a marked increase even at low concentrations. Beck attributes this to the fine dispersion of the oil which, in this case, was nearly colloidal. Changes in the internal friction of an emulsion system evidently depend upon the degree of dispersion of the oil globules. With a predominance of small-sized globules, conditions analogous to those of a colloidal system are obtained; temperature changes and other factors may produce a change in viscosity. The presence of colloids in such an emulsion system may also effect a change.

Monson^{171a} postulated that the viscosity ratio:

$$\frac{\text{viscosity of emulsion at } t^{\circ} \text{ F.}}{\text{viscosity of clean oil at } t^{\circ} \text{ F.}}$$

may be considered as a general index of emulsion stability. Viscosity

ratios were determined for twenty water-in-oil emulsions prepared from five California crude oils, and their maximum viscosity ratios were found to be as in Table 4:

Table 4. Maximum Viscosity Ratios

Crude Oil Water Content (%)	Viscosity Ratio
10	1.3
20	1.8
30	2.7
40	4.1

It was also found that a straight-line viscosity-temperature curve is a good index of the stability of the emulsion. The curves for less stable emulsions were found to bend down at high temperatures, whereas curves of more stable emulsions remained a straight line. Furthermore, if the viscosity ratio of an emulsion gives a relatively straight-line curve for two temperatures, *e.g.*, 100 and 185° F, the viscosity ratio will be more nearly the same at the two temperatures, the more stable the emulsion. If the emulsion is relatively unstable, the ratio for the higher temperature will be considerably lower than that for the lower temperature. The greater the difference between the two temperatures the greater the accuracy of the test.

A change in viscosity has been ascribed by Lipatow¹⁵⁸ to an aggregation of particles, and therefore to a decrease in the degree of dispersion. Two types of processes are offered as an explanation: (1) that of suspensoids, in which the ageing process is combined with a decrease in stability—an irreversible process; and (2) that of emulsoids, in which the ageing process is combined with an increase in viscosity and a decrease in the degree of dispersion with an increase in stability—a reversible process. Suspensoids and emulsoids age for different reasons. Suspensoids change in viscosity because of further aggregation of particles; emulsoids, because of a slow process of hydration, that is, adsorption of water resulting in a change in volume and therefore in the size of the particles. It is Ostwald's opinion^{184, 185, 186} that the time factor is perhaps the greatest variable in the viscosity of hydrated colloids. In all determinations on the viscosity of typical colloids, different values were obtained, depending on the age and the rate at which the temperature changes. Viscosity increases with age and tends to approach a final value, S-shaped curves being obtained.

Einstein's^{61, 62, 63, 64} equation for viscosity:

$$\eta_1 = \eta_0 (1 + 2.5Q)$$

where η_1 η_0 is the viscosity of dispersion and that of the continuous phase and Q the fraction of the total volume which is the disperse phase, postulates that viscosity is a linear function of the concentration of the disperse

phase and independent of the size of the dispersed particles and the distance between them. Hatschek^{113a} based his equation:

$$\eta_1 = \eta_0 \left(1 + \frac{q}{2} f \right)$$

on geometrical principles. In contrast to Einstein's equation, it is applicable to dispersions in which the disperse phase exceeds 50 per cent of the volume of the system. With a rotating cylinder type of viscometer, the viscosity was found to be a function of the speed of rotation below the critical. For velocities above the critical, the following equation holds true:

$$\eta = \frac{\eta_0}{1 - \sqrt[3]{Q}}$$

Hatschek further assumes that the diameters of the particles lie within the limits between which Stokes' formula is applicable; also, that in the case of highly viscous emulsions or emulsoids, a certain phase relation plays an important role, indicating that the content of the disperse phase must be such that the mobility of the disperse phase assumed for the formula no longer exists, and approaches or even exceeds 74 per cent of the disperse phase. This does not hold true. Parallel measurements of viscosity and photomicrographic determinations of the distribution of particle sizes of paraffin emulsions in a one-per cent sodium oleate solution were carried out by Sibree^{248,249} to prove Hatschek's assumption that the viscosity for the same type of emulsion is independent (over a wide range) of the size of particles or particle size distribution. Hatschek's formula for the relationship between concentration and viscosity has been proved by applying comparable constant viscosities.

Brillouin,³⁵ studying Brownian movement in an emulsion having a viscosity 160 times greater than water, showed that this phenomenon may be constant even for a viscosity 3200 times greater. Prior to Brillouin's experiments, Perrin, as well as Bjerrum,¹⁹¹ studied Brownian movement, and proved the principle of equal distribution of kinetic energy in aqueous emulsions of low viscosity.

Bancelin,⁸ in his experiments on a gamboge and mastic suspension, found a discrepancy in Einstein's equation:

$$K' = K (1 + 2.5\phi)$$

which he revised to read:

$$K' = K (1 + 2.9\phi)$$

(based on experimental results obtained), where K' is the viscosity coefficient of the emulsion; K , the viscosity of the pure liquid, and ϕ , the total volume of the suspended particles in a unit volume.

Soap solutions readily yield permanent foams owing to their low surface tension and low viscosity. Plateau^{199,200} defined two viscosities for a liquid capable of foaming, namely, the internal viscosity due to internal friction, and the superficial viscosity which resists the movement

of a body situated in the air/liquid interface. According to the type of viscosity, Plateau classified all liquids and solutions into three classes:

Class 1, in which superficial viscosity is twice the internal viscosity. Example: water and most aqueous solutions.

Class 2, in which superficial viscosity is a fraction of the internal viscosity. Example: alcohol, turpentine, and ether.

Class 3, in which superficial viscosity is many times greater than the internal viscosity. Example: albumin solutions.

In an investigation of the relationship between emulsification and viscosity, Smith²⁵³ pointed out that viscosity at the liquid/liquid interface "interfacial viscosity," and not "superficial" viscosity at the air/liquid interface as measured by Plateau, is of first importance in the study of emulsions. According to Plateau's classification, the viscosity favoring emulsion formation is superficial viscosity, which is greater than internal viscosity. From results presented in Table 5, it is to be expected that liquid paraffin would give the poorest emulsion and benzene the best.

Table 5

Disperse Phase	Interfacial Tension	Dispersion Factor	Interfacial Viscosity
Pure benzene	33.6	1.13	0.0034
Benzene	22.6	1.39	0.024
Liquid paraffin	44.6	1.34	0.020

(Kaolin present in all three cases)

The viscosity of the interfacial film produced when a solid is introduced into the interface has been investigated, using the method of Stables and Wilson^{255a} (refer also to Grotian^{89a}). The various discs (brass, glass, nickel) were suspended in such a way that the interface of the investigated liquids was half-way up the side of the container, the interfacial viscosity observed being the logarithmic decrement.

The best emulsions are formed by kaolin which, as stated, is preferentially wetted by water. In one or two cases solids were found which gave evidence of emulsifying, but showed no appreciable interfacial viscosity. Copper sulfide and lead carbonate are representative examples. On the other hand, aluminum hydroxide and lead chloride have a high interfacial viscosity but a comparatively poor emulsifying ability. Most of the solids chosen were selected from a list prepared by Hofmann¹²³ and Reinders²¹⁹ as being typical of those which tend to collect at the interface. This investigation has shown that solids of good emulsifiability have, as a rule, high interfacial tension.

Very often experimental results do not permit estimating accurately the influence of viscosity for, in most instances, it is difficult, if not impossible, to differentiate between the effect of viscosity and the influence of other factors effecting changes at the same time. When solutes change the viscosity of a liquid, they affect the surface tension at the same time. Clark and Mann,⁴⁵ in a study of the emulsifying ability of sucrose and certain colloids for benzene and kerosene emulsions, made a comparative

study of viscosity and interfacial tension. Commenting on the results which they obtained with sucrose, they are of the opinion that viscosity is of first importance. Dextrin was found to be a better emulsifying agent than starch, but viscosity was found to be of secondary importance. Further, Clark and Mann discuss viscosity from the standpoint of emulsification, and classify it as of two types, namely, that of a molecular dispersoid, which has a true internal viscosity or internal friction resisting any molecular movement, and that of an emulsion, which offers no such resistance. Sugar has a true internal viscosity, or friction, which resists molecular movement, whereas dextrin, starch, gelatin, and albumin, in solutions of equal viscosity, offer no such resistance. These investigators attribute this resistance to the fibrous or granular structure of the gel-forming substances in solution, through the interstices of which colloids or crystalloids pass readily, exhibiting viscosity by virtue of their deformation as measured by the force required to pass through the capillary of a viscometer. Low interfacial tension and high viscosity produce favorable emulsifying conditions in gum-arabic solutions. On the other hand, egg albumen, by far the most effective in emulsification, has the least effect on the viscosity of the system.

Many viscous solutions are poor emulsifiers. Pickering¹⁰³ states that, although high viscosity and low surface tension in a liquid may facilitate the emulsification of an oil, yet emulsion formation may also occur in a liquid which does not possess either of these properties. Further, it is to be understood that a viscous liquid should show a tendency to slow down the coalescence of oil globules but, when interpreted in terms of emulsification, no important role can be ascribed to viscosity. Even the emulsifying ability of dilute soap solutions, which are not viscous, may be destroyed by increasing the concentration, *i.e.*, the viscosity, above a certain point. The insoluble solids which Pickering first used as emulsifying agents would no doubt have very little effect on the viscosity of the liquids emulsified.

Holmes and Child,¹²⁸ from their study on the emulsification of kerosene in an aqueous solution of gelatin, made more or less viscous by the addition of salts, concluded that the most important factor in emulsification of oil in water with the aid of gelatin was not the maximum, but the most favorable viscosity. Although this conclusion refers to gelatin, it may be applied to all highly hydrated compounds.

It has been pointed out by Augustin⁴ that soaps, when used as effective emulsifiers, must be worked up into a viscous mass, for the lighter the emulsion liquid, the less its resistance to emulsification, since there is a relationship between viscosity and the percentage emulsified. If emulsification takes place immediately in a weak soap solution, it is possible to determine emulsification at once by the increase in viscosity. This increase in viscosity upon emulsification Pickering explains as being due to the great increase in the oil/water surface when the oil is reduced to minute globules. Actually, the viscosity of emulsions is independent of particle size. An ordinary emulsion, although containing 70 to 80 per

cent of mobile paraffin oil, is as viscous as thick cream, and its viscosity increases in proportion to the amount of oil present, even when that oil is a very light one, such as benzene. With a very high oil content, the emulsion becomes practically a solid. Viscosity tests of emulsions formed in the laboratory showed a gradation in the emulsified oil ranging from a slightly viscous to a highly viscous, semi-solid emulsion. As the percentage of oil increased, the emulsion became more viscous until a semi-solid, plastic mass was formed.

In the preparation of benzene-in-water emulsions of different concentrations of benzene, using sodium oleate for the oil-in-water type and magnesium oleate for the water-in-oil type, both soaps being a 5-per cent solution, Richardson²²³ effected a homogeneous distribution of particle size of the emulsion system by spraying the components through a hole against a reflection plate. Viscosities were measured with the Couette apparatus, and it was found that emulsions having a very high percentage of disperse phase are almost always solid and, as a result, flowing takes place only above a definite shearing stress. No influence of surface tension on the internal viscosity of the system was noted. An equation based on theoretical principles for the viscosity-concentration function was formulated by Richardson, who is of the opinion that its constant is dependent on shearing stress.

Narayanaswamy and Watson,¹⁷⁷ working with gasoline-in-water emulsions and using the oleates of sodium, triethylammonium and ammonium as emulsifiers, observed that freshly prepared emulsions gave very irregular results with respect to viscosity measurements but, in the absence of air, reproducible values were obtained. The relation between viscosity and composition in most cases is logarithmic in type over a considerable portion of the stable range, but the equation relating concentration and viscosity is not that of Arrhenius.

From the results obtained in a study of pharmaceutical emulsions, Marshall¹⁸¹ concluded that viscosity influenced the size of the emulsion globules and affected their permanence, but otherwise had no theoretical significance. Further, he stated that an increase in the viscosity of an emulsion may be obtained by: (1) increasing the viscosity of the emulsifying agent, that is, by the addition of a gelatinous or a similar substance; (2) decreasing the size of the emulsified globules (the smaller the globules, the greater the viscosity of the emulsion, other things being equal); and (3) adding more material to be emulsified, that is, establishing a greater ratio of dispersed material to the dispersion medium.

Many investigators in the field of emulsions have accepted the conclusion that viscosity aids emulsification solely by virtue of the hindrance offered to coalescence of the dispersed globules, and is not the cause of emulsification. Holmes and Child,¹²⁸ studying the dispersion of kerosene in gelatin solutions as a function of viscosity, as well as the relation of viscosity to emulsion stability, concluded that "viscosity plays the dominant part in the stability of gelatin emulsions" and not the interfacial tension, although they were unable to prove the presence of a film of

gelatin adsorbed at the surface of the kerosene globules. It is easy to confuse the effect of viscosity on the formation of an emulsion and its influence on the stability once the emulsion is formed. However, it is to be expected that high viscosity renders the diffusion of one liquid through another liquid difficult, thereby retarding emulsification, although the rubbing of one phase against the other might, to some extent, aid dispersion. In the work of these investigators, the viscosity of the liquid systems was varied by the addition of salts whose action in causing liquefaction and solidification of gelatin is far more complete than the mere mechanical action of altering the viscosity, for "the leading factor in oil-in-water emulsification with the aid of gelatin is viscosity, not the maximum, but the most favorable viscosity."

It has been reported by Fanto and Spriter⁶⁹ that of the two possible forms of two-phase liquid emulsions, the more stable form is that in which the continuous phase is a liquid showing a high surface viscosity, that is, the one inclined to form a film. The viscosity of the interface may be decreased by the addition of substances employed for the resolution of emulsions. Metcalf¹⁰⁷ stated that when peptone is placed on a water surface, the surface viscosity and the stability increase in the same direction as the thickness of the film. White and Marden²⁸¹ have shown that the viscosity of an emulsion affects its stability. Therefore, concentrated emulsions prepared in soap solutions, using viscous linseed oil, are more stable than the more mobile, liquid kerosene and benzene emulsions prepared in solutions of cane sugar.

It has been shown by Ramsden^{211,213,215} that solid or highly viscous coatings are formed more or less readily on the free surface of all protein solutions capable of forming persistent emulsions without having a high viscosity, and that similar films of viscous matter form at the liquid/liquid interface. Rayleigh^{216,217} observed that the surface tension of fresh soap solutions is frequently greater than that of aged solutions. This phenomenon was also noted with saponin solutions, Rayleigh attributing the reduced surface tension to the presence of an insoluble film on the surface of the aqueous solution. A similar explanation was offered by Marangoni.¹⁶⁰

Broughton and Squires,³⁷ investigating the viscosity of oil-in-water emulsion systems prepared with aqueous solutions of sodium oleate, saponin, and triethanolamine oleate (1, 2, and 3 per cent by weight, respectively) as continuous phases, and Nujol, benzene, and olive oil as disperse phases, found that these emulsions behave as non-Newtonian liquids and that viscosity is not a constant for any given emulsion, but varies with the rate of shearing. These experiments also indicate that the limiting viscosity (the asymptote of the viscosity versus rate of shearing curve) at infinite rate of shearing increases with an increase in the volume concentration of the disperse phase. With respect to the effect of the type of emulsifier/stabilizer employed on the viscosity of a given phase-pair, it has been found that those stabilizers emulsify the best which give emulsions having the lowest limiting viscosity.

Rossi ^{228a} investigated the viscosity of paraffin-oil emulsions in a 3-per cent aqueous sodium oleate solution (pH = 8.9 at 20°), rotating the cylinder type of apparatus used at variable speeds; emulsions of various concentrations, namely, 10, 20, 30, 35, 40, and 50 per cent (by volume of the disperse phase) were measured. Likewise, viscosity measurements were made for emulsions having a pH of 9.3 (by addition of sodium hydroxide). Both sets of emulsions were homogeneous and contained as dispersed particles those having diameters of 1.80-1.85 μ . The results obtained indicate that, whereas the size of the particles affects but little the limiting viscosity value η_{∞} , the size has a considerable effect on the path of the viscosity curves. This was also found to be true of the pH value. To explain this, it is assumed that these factors affect the lyophilic shell surrounding the dispersed particles, and that their action is slight when this shell is highly deformed, *i.e.*, when the zones in the immediate area of the surfaces of the particles enter into play. Within the range of velocities used in the experiments, practically all emulsions appeared to conform to the relation expressed in the following equation:

$$\pi = \pi_{\infty} + (K/\Omega)(1 - e^{-\alpha\Omega})$$

The properties of the investigated lyophilic emulsions were found to be better represented by the values of the constant K in the equation than by their viscosities measured at very high velocities.

✓ The emulsification and stabilization of emulsions as a function of viscosity clearly shows that viscosity, in some cases, actually does favor the permanence of the system and, indirectly, emulsification; in other cases, it does not, depending on the nature of the system. Often substances added as emulsifying agents not only change the viscosity of the system, but also affect other properties, for instance, particle size and emulsifying ability; they even cause chemical changes. The most plausible explanation of the effect of viscosity on emulsification and in contributing to the permanence of the system apparently is the one given by Bancroft, as well as Hillyer, namely, that viscosity is not the cause of emulsification, but aids it, in some cases solely by virtue of the hindrance offered to the coalescence of the dispersed globules, and that, because of the high internal viscosity, the thinning of the invisible film separating the globules is so slow as to render the emulsion system permanent. The viscosity factor may also enter into the mechanism of emulsion formation with regard to decreasing the rate of adsorption. In the resolution of emulsions, viscosity may decrease the mobility of the droplets constituting the disperse phase, thereby retarding their approach and coalescence.

Solubility

Emulsification without an emulsifier has been considered possible. Groschuff ⁸⁹ claims to have prepared very dilute emulsions of water in benzene and mineral oils by heating the water and oil in a sealed tube and then cooling to 18° C. The emulsion in benzene was stable for a few

minutes, that in petroleum for one hour, while paraffin oil, and particularly transformer oil, gave stable emulsions. There is no evidence that emulsifying agents were absent from the petroleum oils tried. Similar results were published by Hall.⁹⁴ In the experiments conducted by Pickering,^{193,194} very concentrated emulsions were prepared when even 99 per cent by volume of oil was emulsified in dilute soap solution.

Emulsions containing as much as 99 per cent of ordinary illuminating oil have been obtained, the remainder being a one-per cent soap solution. Such strong emulsions, however, cannot be obtained directly; they must be prepared by taking a weak emulsion and gradually increasing the oil content, churning it after each addition. Even these strong emulsions may be considered true oil emulsions. Any emulsion (even 99 per cent) will mix perfectly with water to form a weak emulsion, but will not mix with more paraffin unless that paraffin is emulsified with it by further churning. An ordinary emulsion, although containing 70 to 80 per cent of mobile paraffin oil, is as viscid as thick cream, and its viscosity increases with the proportion of oil present, even when that oil is a very light one, such as benzine. With a very high percentage of oil, the emulsion becomes practically solid, resembling blanc mange. When paraffin oil is churned with a solution of soft soap, an emulsion is formed which rises to the surface and generally contains 65 to 82 per cent by volume of oil. Emulsions containing as much as 99 per cent by volume of oil can, however, be obtained, but these are so stiff as to be almost solid. The character of the oil does not greatly affect the results; neither does the extent of churning, nor the proportion of soap, so long as this proportion is within certain limits.¹⁹²

Lewis^{151,152} states that in the absence of an emulsifying agent emulsions of oil in water may be made up to a maximum concentration of 2 per cent. Usually, oil-in-water emulsions without an emulsifier are very dilute (oil content, 1 part in 10,000), so that in practice they are of little significance. This investigator also claims that if a small amount of oil is boiled with water in a reflux condenser, a dilute emulsion may be obtained. Clayton is of the opinion that a knowledge of the mechanism of solubility of emulsions is insufficient to account for the fact that in general pure two-phase systems appear to be stable only over low concentration ranges. It has been suggested by Berkman, as well as by Egloff, that the preparation of two-component emulsions may be possible, but only under certain conditions of emulsification, provided the disperse phase is in a very fine degree of division. For example, when oil and water are forced through fine capillaries under high pressure, a stable emulsion results. In practice, stable emulsions are usually formed in the presence of an emulsifying agent.

The nature and function of an emulsifying agent greatly influences emulsification. It is Wilson's belief²⁸⁶ that an emulsifier has two distinct functions: (1) to lower the interfacial tension, and (2) to stabilize the emulsion first formed. Emulsifying agents are of two types, namely, molecular or colloidal solutions, and finely divided solids in suspension.

However, no particular experimental study has been made of emulsifying agents in molecular solutions; in fact, it is generally believed that emulsifying agents, with the exception of the fine-grained precipitates first used by Pickering, must be colloiddally dispersed. The emulsifying agent may be added as a suspension to the internal phase, dispersed in the continuous phase, or formed by chemical action at the interface. Moreover, two cases must be differentiated: (1) that in which a substance (emulsifier) having naturally colloiddal properties is added to the emulsified system and, under the existing conditions of the system and in the presence of electrolytes or with changes in temperature, etc., becomes a molecular solution; (2) that in which a molecularly dissolved emulsifier transforms the molecular component present in the emulsion into the colloiddal state.

A third group of emulsifiers, usually soaps, which are classified as a special group of colloids called colloid-electrolytes, includes systems in which equilibrium exists between molecularly and colloiddally dispersed parts. In most cases, this equilibrium is displaced by two factors, namely, temperature and concentration, and this fact complicates the conditions existing in an emulsion which has been emulsified and stabilized with soap. If soaps present as emulsifiers are colloiddally dispersed, as is so often indicated in the literature, then the question arises why it has not been proved (often colloiddally dispersed soaps, as seen under the ultra-microscope, using the Szegvary diaphragm, show distinctly long thread-like particles in addition to the usual round particles).

According to Friedel,⁷⁵ soaps are in the "smectic" state, which is a mesophase of liquid crystals. It is important to know that only soaps of rather high concentration are colloiddally dispersed, whereas very small amounts of soap can act as good emulsifiers, irrespective of the colloiddal nature of the soap. The assumption that emulsifying agents are always colloiddally dispersed is incorrect. It must be pointed out that even a substance in a colloiddal state, when added to a new system, sometimes retains and sometimes loses its colloiddal properties, depending on the type of system to which it has been added and the physical factors involved. In an emulsion stabilized with soap, there are to be considered not only the dispersion of one liquid in another, but also the soap-in-oil and soap-in-water solution systems, together with their respective equilibrium factors. Moreover, commercial soaps used as emulsifiers contain various fatty acids which may produce their own emulsoids. By diluting such soap solutions with water, the molecules may partly split up into fatty acids and caustic. This hydrolysis apparently has an important bearing on the behavior of an emulsion system.

There is very little difference between potassium soaps and sodium soaps in solution, except that the former are rather colloiddally dispersed, solidify at much lower temperatures, and possess a greater tendency to exist as transparent liquids, which are often very viscous. To obtain the same solidification or crystallization as with sodium soaps, higher concentrations of potassium soaps having a greater carbon content must be used and, in addition, a much lower temperature. Potassium soaps are

more soluble than the corresponding sodium soaps. As a rule, soap solutions which readily crystallize can be easily salted out with concentrated salt solutions. McBain¹⁶⁵ advanced the theory that soap solutions are salts in which an ion is replaced by an ionic micelle exhibiting high electric conduction and great solvation, and that they carry a large number of electric charges. While very low concentrations may result in the formation of simple electrolytes, high concentrations or the addition of other substances may lead to the formation of a neutral colloid. This ionic micelle of high valence and hydration explains the high conductivity and viscosity of colloidal electrolytes. Concerning the constitution of soap solutions, it may be said that, when very dilute soaps are partially hydrolyzed, the resulting product is either in a coarse or a colloidal suspension and consists of a neutral salt (NaR) and an acid soap (NaHR_2), where R is the radical of the fatty acid.

All soap solutions contain free hydroxyl ions. For example, in a tenth normal solution in which soaps are used as emulsifiers, soaps are composed chiefly of simple electrolytes in molecular solution with simple ions, and the hydroxyl ion concentration is about $1/1000N$. As the concentration increases, the fatty acid ions rapidly coalesce and form ionic micelles. In a $\frac{1}{2}N$ or a $1N$ solution, the colloidal electrolyte comprises all the soap. Alcoholic soap solutions are entirely different in their behavior, for the soap is present throughout the concentration range as an unhydrolyzed electrolyte.

Kremnew and Papkowa-Kwitzel¹³⁹ found that the greater the hydration of alkali cations ($\text{Li} > \text{Na} > \text{K} > \text{Rb}$), the greater the decrease in the emulsibility of sodium oleate. This is also true of anions of sodium salts, as well as of acids ($\text{SO}_4 > \text{Cl} > \text{NO}_3$), and applies equally well to alkaline-earth cations ($\text{Mg} > \text{Ca} > \text{Ba}$). For low salt concentrations, a maximum increase in the emulsibility of sodium oleate takes place, as the result of a retardation in the hydrolysis of soap through neutral salts. Further, these investigators attribute the slow decrease in the emulsifying ability of high concentrations of electrolytes to the dehydrating action of the added ions (cations and anions) on the soap, which becomes more hydrophobic. This "hydrophobization" is interpreted as a reaction in which the soap and acid molecules form complex compounds while accumulating reciprocally with their polar groups. The addition of electrolytes, however, decreases the hydration "covers" of these groups and thus exerts a lyotropic influence which Kruyt and Edelman^{139a} designate as an "action at a distance." This lyotropic "effect" is due to the hydrophobization of alkali soaps in which the association of molecules plays a significant part.

An emulsifying agent in most cases is molecularly or colloiddally soluble, either in one or both liquids which it emulsifies. The liquid which dissolves the emulsifier generally forms the external phase. Emulsifying substances soluble in water have the tendency to form oil-in-water emulsions, while those soluble in oil form emulsions of the reverse type. Two principal factors enter into the discussion of an emulsifier, namely, that

the emulsifying power is related to the colloidal state of the emulsifying agent, and that the phase in which it is soluble becomes the continuous, not the discontinuous, phase. If the emulsifying agent goes into a colloidal solution in one phase, but is precipitated by the other then, according to Padgett,¹⁸⁸ the latter phase is dispersed, making possible the formation of a water-in-oil or an oil-in-water emulsion, depending upon whether or not the emulsifying agent is a hydrophobic or a hydrophilic colloid.

Bancroft,^{9,10} commenting on Höber's assertion, states, "had he been considering the general problem, he would probably have made the statement that an oleophilic colloid should be used as an emulsifier, if it is desired to prepare an emulsion of water-in-oil." This statement, expressed otherwise, declares that if liquids *A* and *B* are to be emulsified, and the emulsifying agent is more easily peptized, that is, subdivided into particles of colloidal size, by liquid *A*, then liquid *B* will be dispersed.

In an investigation of soaps of low molecular weight fatty acids conducted under varying conditions of temperature, concentration, and medium of reaction and in different solvents, such as acetates, propionates, butyrates and valerates, it was found by Mayer, Schaeffer and Terroine¹⁶³ that even in saturated solutions at 18° C no colloidal characteristics, such as transmission of light, presence of ultramicroscopic particles, or diffusion through a permeable membrane such as collodion were seen, whereas solutions of 0.1*N* sodium caprylate showed a slight diffusion of light and indicated the presence of ultramicroscopic particles (the normal solution shows a great number of ultramicroscopic particles). Saturated solutions of sodium laurate, sodium palmitate, and sodium stearate exhibit the same phenomena. These substances are completely hydrolyzed by dialysis over a long period of time, and for the same soap the colloidal character is more apparent, depending upon the transition from a neutral solution to an alkaline or an acid solution. The appearance of the colloidal state in soaps is attributed by these investigators to hydrolysis occurring in aqueous solutions. The low molecular weight series of fatty acids gives all possible combinations with water, and those soaps which are in molecular solution are miscible with water. The middle members of the fatty acid series are liquid and not miscible with water, giving two-phase solutions and some turbidity. The size of the dispersed globules increases with the addition of acid, whereas the addition of alkali decreases it, but the globules do not disappear, an ultramicroscopic suspension of soap being formed instead. The higher members of the fatty acid series, which are more or less soluble, show ultramicroscopic or microscopic particles, and precipitate on addition of strong acids, giving ultramicroscopic suspensions; addition of alkalies causes formation of high molecular weight soaps. When a fatty acid soap is displaced by an acid, the upper phase passes from the suspended to the agglomerate state, and the middle phase from a molecular solution to an ultramicroscopic suspension (the precipitation of the external phase apparently does not cause any modification).

Gurwitsch⁹¹ believes there is a reason for the varying behavior of soaps in aqueous or alcoholic solutions as observed in the colloidal character of aqueous soap solutions because other colloiddally dispersed substances, such as gelatin, casein, water-soluble gums and resins, as well as resins, asphalts, and naphthenic soaps which occur in crude oils, show a similar action, that is, the surface tension decreases markedly at the oil-water interface and occasionally these substances show a great tendency to emulsify. Donnan and Potts,⁵⁹ as well as Krafft,¹³⁶ stated that the emulsifying power of the fatty acid salts begins at the point at which formation of colloidal solutions starts. It is Brigg's opinion²⁰ that in every case the investigation has shown the apparently soluble emulsifier to be in colloidal suspension in the external phase of the emulsion.

In an investigation of emulsions prepared with iodine, Holmes and Cameron¹²⁷ found that this halogen has an emulsifying ability only when in the colloidal state. This phenomenon is not shown by bromine or chlorine, nor by such salts as sodium iodide or calcium iodide (evidently a film of colloidal aggregates of iodine is formed at the liquid/liquid interface). von Ammag^{274, 275} observed that reddish-brown solutions of iodine in carbon disulfide, carbon tetrachloride, chloroform, and petroleum showed practically no ultramicroscopic particles, whereas colloidal aggregates of iodine were readily found in amyl acetate solutions and in amyl alcohol. Emulsification of carbon disulfide, carbon tetrachloride, and chloroform in water, using iodine as an emulsifier, was unsuccessful, whereas emulsions of amyl alcohol, amyl acetate, and ethyl acetate dispersed in water were readily prepared with the aid of iodine. The film formed is a Gibbs adsorption film rather than one of mere precipitation. However, it is Hildebrand's contention¹²⁰ that the brown color of certain iodine solutions is due to the formation of iodine compounds. While many investigators are of the opinion that an emulsifier must be a colloid by nature, or be present in the emulsion in a colloidal state, there are many exceptions.

Clark and Mann,⁴⁵ in a study of the emulsifying efficiency of sucrose for benzene and kerosene emulsions, state that though sugar furnishes a large and favorable viscosity, it does not compare as an emulsifying agent with even minute concentrations of other substances in which the viscosity factor is practically negligible. That aqueous solutions of alcohol and alkali salts of higher fatty acids are present not only in the colloidal state, but also in the form of simple molecules, and therefore fail to lower the surface tension and show a tendency to emulsify, has been shown by Krafft.¹³⁶ The same apparently holds true for the sulfonic acids formed from crude-oil products obtained by sulfuric acid refining. In aqueous solutions they are present in the free state and also as colloiddally dispersed alkali salts, as indicated by the ease with which they are salted out and their tendency to foam. When a sufficient amount of alcohol is added, the colloidal complexes are split into simple molecules and sulfonic acids and their salts lose their emulsifying power.

It is the opinion of Holmes¹²⁶ and of Holmes and Williams¹³¹ that

polyvalent alcohols are not useful as emulsifiers. While methyl and ethyl alcohols, as well as allyl alcohol, are able to emulsify benzene in water, phenol and resorcinol were found to be more satisfactory; naphthols and benzyl alcohol are not satisfactory. Experiments carried out with acids showed that the activity of all fatty acids up to caprylic was similar to that of aromatic sulfonic acids. A more favorable action was noted for the sodium salt of β -naphthol sulfonic acid than for the free acid. Esters, aldehydes, ketones, and nitriles exhibit no special phenomena when used for emulsification. A great difference exists between the emulsifying ability of soaps and those of the low molecular weight alcohols; but it is important to know that certain substances in molecular solution do form emulsion films. According to these investigators, film formation is due to the aggregation of alcohol in benzene, in which water should be the disperse phase; actually, it is the benzene that is dispersed. Proteins and soaps are polar compounds, the molecules of which form large colloidal aggregates because of their attraction by both phases; therefore their films have greater strength in emulsions.

It would be difficult to describe at length the behavior of the many substances which have been investigated with regard to their emulsifying ability. Thus far, no systematic attempt has been made to arrange all the emulsifiers in the order of their ability to promote and maintain stable emulsions,²⁵² but they may be classified roughly into three groups, namely, those which give true emulsions, those which form imperfect or quasi-emulsions, and those which do not emulsify at all. Good emulsifying agents are soluble or partially soluble substances, among which may be mentioned soft soaps, soluble starch, milk, glue, egg albumen, saponin, and quillaia bark (soap bark), suitable when the proportion of oil present is not large. Other emulsifiers are calcium carbonate, calcium arsenate, lead arsenate, freshly precipitated zinc oxychloride or basic zinc chloride, fine, dry unheated clays, such as Oxford clay, ferrous hydrosulfide, glycerol,⁵ and rosin¹¹ for emulsification of water in benzene; sodium resinate (pure resin soap)³³ is not so effective as sodium oleate for emulsifying benzene in water; gum dammar is suitable for¹²⁷ water-in-oil emulsions, and precipitated hard or soda soaps.

Gelatin, casein, gum arabic and all the so-called "solvated colloids" are also good emulsifiers, producing oil-in-water emulsions; lanolin and oil-soluble cholesterol produce water-in-oil emulsions. Water-soluble sodium and potassium soaps are among the best emulsifying agents for oil-in-water emulsions; and soaps of the alkaline earths and of iron, zinc, and aluminum, are oil-soluble and normally form emulsions of the water-in-oil type. Sucrose⁴⁵ has been recommended for oil-in-water emulsions; finely divided red lead¹²³ for emulsions of chloroform in water; sodium oleate and magnesium oleate¹⁹⁰ for emulsifying in water the highly-purified mineral oil known as "Nujol"; sulfonated stearic acid and sulfonated palmitic acid^{149,150} for emulsions of oils, fats, and waxes in water; sodium salts of sulfonic acid²⁷ for emulsifying mineral oils; lead sulfate²⁴² for emulsifying nitrobenzene in mineral acids; montan wax²²⁷ for

water in petroleum; and kieselguhr¹⁴⁶ as an emulsifying agent in the study of the reduction of emulsified nitro-compounds.

Weichherz,^{277, 278} in the first of a series of papers, discusses the influence of the soap content of the two phases on the kind of emulsion obtained, that is, high concentrations of soap promote water-in-oil emulsions and low concentrations effect oil-in-water emulsions. In a later paper, Weichherz and Pletnjewa²⁷⁹ deal with the system xylene/phenol/sodium oleate/water, choosing an arbitrary ratio of the first three components and adding varying amounts of water. Although similar emulsion systems may be formed by substituting phenol through *o*-, *m*-, or *p*-cresol, cyclohexanol, *p*-nitrophenol, *p*-amidophenol, hydroquinone, benzyl, methyl, ethyl, propyl, isobutyl, or isoamyl alcohol, as well as acetone, they appear to be stable only by using phenol as a diluent, or a higher concentration of sodium oleate.

Crude oils containing resins, asphalts, and naphthenic acids or soaps are oil-soluble and give rise to emulsions in which water is the disperse phase. In some crude-oil emulsions, oil is the disperse phase. On the other hand, it has been pointed out by Finkle, Draper and Hildebrand⁷⁰ that oleic and stearic acids, soluble in benzene and practically insoluble in water, do not give rise to water-in-oil emulsions according to the accepted theory; instead, they form unstable emulsions of the oil-in-water type, benzene being the disperse phase.

The rule that the emulsifying agent must be dissolved in the external phase holds for the majority of emulsifiers, but does not cover all of them. Holmes and Williams⁹⁵ state that it must not be assumed that any substance soluble in both benzene and water and causing a decided lowering of the interfacial tension will act as a good emulsifier. Acetone, for example, is soluble in both these liquids and yet shows no emulsifying ability; neither does methylethyl ketone. Iodine, as reported by Holmes, when shaken with water and ether, dissolves in the ether and at the same time forms an ether-in-water emulsion.

There is no single rule which determines whether a good emulsifier should be soluble, whether it should always be present in the external phase, or whether it should always be in the colloidal state in order to effect emulsification. From the information given, it may be seen that in some systems the emulsifying agent is molecularly soluble, in others, colloiddally dispersible; but Bancroft's rule that the phase containing the emulsifying agent is external is now generally accepted.

Hydration

Fischer^{72, 73} proposed a theory of emulsification known as the hydration theory, according to which emulsions can be produced only when the liquid which is to become the continuous phase is used in the formation of a hydrated compound of the emulsifying agent employed. Also, "when it is said that the addition of soap favors the formation and stabilization of a dispersion of oil-in-water, it really means that soap is a hydrophilic colloid which, with water, forms a colloid hydrate with certain physical

characteristics, and that the oil is dispersed in this." Fischer attributes the emulsifying efficiency of gum arabic, gelatin, casein, dextrin, agar-agar, and albumins to their ability to form colloidal hydrates, and their degree of emulsion formation to their degree of hydration. Further, he assumes that the amount of emulsifier present in the emulsion produced should be sufficient to combine all water available, if a permanent system is to be produced. As evidence for his assumption, Fischer states that a neutral casein solution is not a good emulsifying agent, neither is it in a hydrated form; but when acidified or made alkaline, it becomes hydrophilic and possesses emulsifying properties. It is also thought that the acid or alkaline condition affects the electric properties of the casein molecule and therefore contributes to its emulsifying ability.

The work of Fischer does not point out that changes in an emulsion system subjected to hydration are always accompanied by changes in the electric charge. These two factors go hand in hand. By hydration of an emulsion is understood the tendency of an emulsifying agent, that is, a colloiddally dispersed substance, to adsorb water on the surface or to combine with water to form a hydrate, the amount of water adsorbed depending upon the adsorbing surface and/or the degree of dispersion. In the precipitation of a hydrated colloid, dehydration is accompanied first by an increase in the degree of dispersion, followed by the formation of large aggregates of the dehydrated colloidal particles. These dehydrated colloidal particles present in the disperse phase are electrically charged, and their electric discharge causes precipitation; in fact, there is a superposition of dehydration and electric discharge.

Dehydration, as shown by experiments with hydrated sols, does not depend to a great extent on the electric properties of a substance, so that electric phenomena play only a minor role; nevertheless, they must be taken into consideration. On the other hand, it is a fact that some emulsifiers are true hydrated colloids, while others emulsify without being hydrated. Sherrick,^{244, 245} in his article on "Oil Field Emulsions—How to Eliminate Them," stated that the action of certain commercial treating compounds is probably due to the fact that they are hydrophilic colloids. A hydrophobic colloid should discharge an emulsion formed by the use of a hydrophilic colloid and a hydrophilic colloid should discharge an emulsion formed by the use of a hydrophobic colloid. As a corollary, Bancroft stated that "a hydrophilic colloid will tend to make water the dispersion phase, while a hydrophobic colloid will tend to make water the disperse phase."

In experiments with emulsions and gels of vegetable and mineral oils, using tragacanth and gum acacia as emulsifying agents, Krantz and Gordon^{137, 138} attempted to confirm Fischer's hydration hypothesis of emulsification, which postulates that oil is permanently emulsified by a hydrophilic colloid when a sufficient amount of water is present to form a hydrate. In the use of tragacanth, the amount of water taken up appears to be a function of the hydrogen-ion concentration. The range of greatest stability for either vegetable- or mineral-oil emulsions prepared with

tragacanth is from pH 1.9-2.3. The pH range in which tragacanth shows the greatest degree of hydration is, at the same time, the most stable range for emulsions prepared with this substance. However, these investigators point out that by changing the hydrogen-ion concentration of these emulsions, changes in particle size, as well as in the viscosity of the system, are also brought about.

Crockett and Oesper⁵⁰ found that tragacanth is very much inferior to gum arabic in the formation of pharmaceutical emulsions. Roon and Oesper,²²⁸ claiming experimental confirmation of Fischer's hydration hypothesis, obtained similar results in their study of such preparations, and found that a definite ratio of oil and gum to water is necessary; otherwise either less stable emulsions will result, or no emulsification will occur. Gum previously hydrated also inhibits emulsion formation. From their method of preparing this type of emulsion, they concluded that "the agitation disperses the internal phase and the resulting droplets are immediately coated with a hydrated colloid formed at the same instant, this coating being a necessity for emulsification." Further, they assumed that the presence of a hydrated compound is essential to emulsification, and that this substance is most efficiently utilized if formed simultaneously with the dispersion of the oil phase.

The experiments of Roon and Oesper were repeated by Briggs, Du Cassé and Clarke,³⁴ who found that shaking, rather than rubbing or grinding, the substances together gave more latitude in the formation of an emulsion. They showed that olive oil is more readily dispersed in a solution of hydrated gum arabic if first rubbed with a finely divided solid, such as sand, and that such a solid, easily wetted by water, is most efficient and acts best when suspended in the oil phase, since the aqueous phase has a tendency to displace oil from the surface of the solid particles, thereby assisting in the disintegration of the oil. Briggs, Du Cassé and Clarke have abandoned the hydration theory, for they believe that the most important factor in Roon and Oesper's emulsification method is the presence of finely divided solids which increase the area of the interface between oil and water or between oil and solution. Gum arabic has two functions, namely, as a finely divided solid and as an emulsifying agent.

Friedman and Evans,⁸⁰ investigating the influence of pH upon the stability of gelatin emulsions, found a maximum at the iso-electric point. The addition of acid decreases the stability and at pH 2.5 there is another maximum; a further addition of acid again decreases the stability. The addition of alkali also decreases stability, and at a pH 10 a maximum is again obtained; a further addition of alkali rapidly decreases the stability. The dependence of stability on the pH of an emulsion is parallel to that of the surface tension and the viscosity of a gelatin solution. Gelatin has been found to be strongly adsorbed at the boundary surface of a stable emulsion, indicating that hydration as such may be significant, but not of great importance among the factors influencing emulsification.

Zhukow and Buschmakin,²⁰⁶ studying emulsification of benzene and water by means of gelatin, assumed surface tension to be the main factor in the stability of these emulsions (the minimum surface tension corresponds to the maximum stability and the breaks in the surface tension-stability curve to pH 2.5 and pH 9.5, respectively). At the same points lies the maximum dissociation of salts formed by gelatin with acid or alkali, and these maxima correspond to the highest hydration of the ionized particles of gelatin, while the un-ionized particles at the iso-electric point are less hydrated. Zhukow and Buschmakin concluded therefrom that the maximum surface tension at the iso-electric point is in accordance with the fact that gelatin is in the form of unhydrated and undissociated particles. These investigators believe that unhydrated gelatin molecules are most effective as emulsifiers.

Liesegang¹⁵⁵ states that Fischer pointed out that all organic colloids, such as gelatin, agar-agar, starch, and dextrin, which bind water in a suitable manner or are hydrated, stabilize olive-oil emulsions. According to Fischer, the hydrated colloids, to which the soaps also belong, are necessary when the oil concentration increases. The same is true of gum-water emulsions in which all the water is combined with the gum. Liesegang, criticizing Fischer's work, says that the resultant emulsion cannot be considered as an emulsion of oil in water, but as one of oil in a hydrated colloid. Fischer assumes, says Liesegang, that this emulsion can be diluted with a certain amount of water, and therefore his requirement for the complete binding of the water with the gum is hyperbolic. No statement can be made contradicting the possibility that gum is distributed in the emulsion, so that Fischer's requirement is fulfilled by spontaneous contact with the oil drops, *i.e.*, by the presence in the interface of much of the gum and relatively little of the water. Further, Liesegang draws attention to the fact that this method of emulsification does not hold when large amounts of water are added gradually at the beginning.

Clayton⁴⁶ is of the opinion that the work of Fischer does not establish a strong case for his hydration theory, which appears to be particularly one-sided in its treatment of emulsions. According to this investigator, it is sufficient to emphasize the importance of hydrophilic colloids in preparing emulsions of the oil-in-water type, but it is only logical to broaden this scope and to argue that oil-soluble colloids promote the formation of water-in-oil emulsions. The conditions under which water-in-oil emulsions are formed have not been discussed by Fischer, except in certain cases in which he believes there is a critical point at which any attempt to increase the oil content of the emulsions causes them to revert to emulsions of the water-in-oil type. Clayton also claims that Fischer denied the existence of concentrated emulsions such as Pickering prepared with solid emulsifiers.

Fischer's explanation may be plausible, but the role which water plays, compared with that of the disperse phase and the emulsifier, is important. Hydrophilic and hydrophobic colloids, when used as emulsi-

fiers, can be easily differentiated by their action in emulsion formation. The existence of hydrophobic and hydrophilic emulsions is evidenced by the difference in their properties. But Fischer's conclusions that oil cannot be emulsified by a colloid until a minimum amount of water is present and, conversely, that if too much water is present, exceeding the amount of water used in hydrating colloids, no stable emulsion can be formed, are incorrect. Likewise, it is difficult to understand how a one-per cent soap solution can be considered sufficient to form an oil-in-water emulsion in which the soap is combined with all the water present to form any kind of hydrate.

Volume Relation

It is a fact that in some systems there is a mathematical limit of 74 per cent for closely-packed, uniform, rigid spheres in a given space. Pickering,¹⁹² however, recognized that globules in emulsions are not uniform, and also are separated from one another by a film of appreciable thickness. From these facts he concluded that "there does not appear to be any reason why the ratio of the volume of oil to the total volume of emulsion should be of any particular magnitude." But Pickering did not emphasize that it is the distortion of spheres that causes the percentage of internal phase to vary widely from the theoretical limits. A few years later, Ostwald^{184, 185, 186} pointed out that the chief factor concerned in emulsion formation is the proportion of the two phases constituting the emulsion system. Although an oil-in-water system may be formed from a little oil and much water, and a water-in-oil system from a little water and much oil, there exists a concentration range where both types of emulsion are possible. According to this theory, "when to an emulsion of oil-in-water oil is gradually added, the distance between the globules of oil becomes less and less, until finally the globules touch and coalesce, then becoming the continuous phase, enclosing globules of water." Inversion marks a "critical point." If water is added to an emulsion of water-in-oil, another critical point is reached. According to Ostwald's calculation, the majority of all possible mixtures falls into two groups, and the mixture relation lies between 0.221:0.779 and 0.779:0.221.

Ostwald determined the volume relations of equal-sized globules when touching one another, basing his work on the fact that the closest contact of equal-sized globules occurs when three globules, assembled at one point and touching one another are simultaneously touched by a fourth globule. In order to simplify the calculation, Ostwald chose the tetrahedron formed by the contact of four globules, the volume of the tetrahedron having a side equal to $2r$, and referred to as the unit of volume occupied by the emulsion. The volume of the disperse phase at the critical point is given by the sum of the wedge-shaped sections which fill in the angles of the tetrahedron. Therefore, the volume of the disperse phase at the critical point is equal to the difference between the volume of the tetrahedron and the total volume of the wedge-shaped sections

enclosed by the surfaces of the tetrahedron and the globules. From Ostwald's determinations it is assumed that globules of uniform size make up the disperse phase, and therefore the volume occupied by closely packed globules of the same diameter is 74.048 per cent of the total available volume, this percentage being independent of their size.

Thomas^{266, 267} states that if globules of an emulsion are uniform in size then, according as the spheres are packed together as in Fig. 2A or 2B, the ratio of the volume of the internal/external phase will be 52:48 or 74:26.

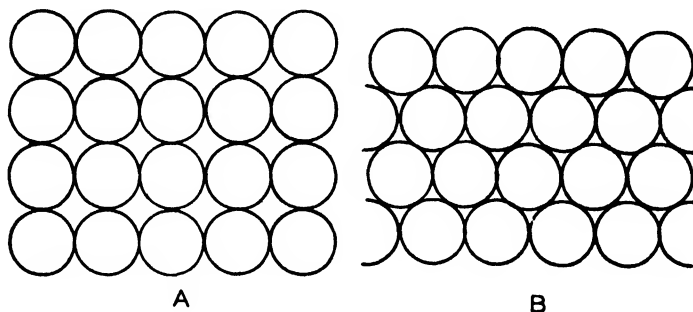


FIG. 2. Packing of Spheres (Thomas²⁶⁶).

In Beijerinck's article,¹⁹ "Emulsion Formation by the Mixing of Aqueous Solutions of Certain Gelatinizing Colloids," attention is drawn to the fact that Ostwald miscalculated the critical relations of the theoretically possible emulsions having equal-sized globules, and that the critical volume relation between the disperse and the continuous phase is not 77.9:22.1, but 74.04:25.96. Further, Beijerinck states that, although the theoretical determinations and practical results of Ostwald's work are not influenced by this numerical error, yet the assumption on which he based his calculation, *i.e.*, the characteristic tetrahedron composed of globules of equal size touching one another and corresponding to the unit volume of a theoretical emulsion, is incorrect, because when a plane surface of globules is covered with a second layer, the boundary surfaces formed by three globules do not touch one another at every point, and this takes place only in every other instance. It is the belief of this investigator that when 74.048 per cent of the internal phase is exceeded, the globules touch one another and coalesce, thereby breaking the emulsion. Further, Beijerinck reasons that when the proportion of either of the two liquids ranges between 0 and 26 per cent, the only type of emulsion possible is that in which this liquid constitutes the internal phase. If either liquid is made up to 26 to 74 per cent of the whole, two types of emulsions are possible. For example, 98 per cent water and 2 per cent oil can give only an oil-in-water emulsion, while 97 per cent oil and 3 per cent water form a water-in-oil emulsion.

Ostwald thought that his hypothesis is confirmed by the fact that when oil is added to emulsions of tar-oil in water prepared with various emulsifying agents, a critical point at which the phases reversed (at about the percentage composition predicted by his theory) was noted for each emulsion. Similarly, on adding water to a water-in-oil emulsion, a second critical point was observed. Ostwald's theory is mathematical and absolute in character, but is not an emulsion theory. Since the spheres of emulsion globules are actually unequal and readily distorted and the interfaces armored, deviations from the mathematical rule are not without exception. Cases have been reported in which the phase ratio apparently determined the type of dispersion formed, so that either an oil-in-water or a water-in-oil dispersion could be produced by varying the proportions of the phases.

It has been indicated by Zhukov and Buschmakín²⁹⁶ that an optimum volume relation corresponding to a ratio of 1:1 exists for the formation of stable emulsions of benzene and gelatin solutions. If to two parts of a one-per cent gelatin solution at 30° is added one part or less of benzene, an unstable benzene-in-gelatin emulsion results, which disintegrates as soon as shaking of the solutions is discontinued. If two parts of benzene and one part of gelatin are taken, then an emulsion of gelatin in benzene results after shaking, which is also unstable. One part of gelatin solution added to one part of benzene solution gives a white, creamy emulsion of benzene in gelatin. These investigators point out that if all the components of an emulsion are poured together and shaken, the type of dispersion formed depends on the volume relation of the components and not on the nature of the emulsifier. If the preparation of an emulsion starts with the ratio of 1:1, and one of the components is added in portions, the type of emulsion formed depends only on the nature of the emulsifier and not on the volume relation. Therefore, it is concluded that the ratio of 1:1 is an optimum condition for the formation of emulsions. This optimum ratio is only approximately indicated, and is displaced in the presence of varying amounts of the emulsifier. These same facts are also shown in the work of Sanyal and Yoshi,²³⁰ who claimed that the ratio also depends upon the density of the oil used.

The conditions governing the type of emulsion produced by merely changing the volume ratio of the two phases were investigated by Sanyal and Yoshi,²³⁰ who experimented with systems of olive oil in water plus 0.02 and 1.0 per cent sodium oleate, and castor oil in water plus 0.1 and 0.2 per cent of sodium oleate. The results of their investigations indicate that water-in-oil emulsions, with light oils like kerosene and benzene, are not stable when large quantities of oil are churned with small quantities of soap solution. On increasing the concentration of the soap solution to about one per cent, the nature of the emulsifying agent is more effective than the volume ratio. However, there is no doubt that a water-in-oil emulsion is formed when the concentration of the emulsifying agent is less than one per cent and the oil used is viscous. In this case, the volume

of the two phases becomes an important factor in determining the type of emulsion.

Robertson,²²⁶ in his study of inversion by the alteration of volume concentration in the case of olive-oil emulsions, giving special attention to "the influence of the proportion of alkali to the total volume of emulsion upon the critical ratio of water to oil at which the emulsion changed character and ceased to be an oil-in-water emulsion," concluded that distilled water does not form stable emulsions with olive oil, stability being given by the action of alkali on the fatty acids of the oil; therefore, stability indirectly depends on the amount of fatty acids present in the oil. Robertson, using pure California olive oil containing only traces of free fatty acids, found that the critical ratio was 7.5:92.5 for 1/2*N* sodium hydroxide (error in calculating, $\pm \frac{0.5}{92.5}$); 9.5:90.5 for 5*N*, and 13.5:86.5 for 1/4*N* and 1/6*N*; no stable oil-in-water emulsion formed using 1/8*N*. Robertson explained this fact by stating that as long as alkali is present in excess, *i.e.*, in an amount greater than necessary for the neutralization of the acid present, the amount of soap formed will be constant; but when the alkali is less, the amount of soap formed will be proportional to the alkali present, resulting in a gradual decrease in the concentration of the soap; the ability of water to surround the oil globules also decreases. Therefore, when the critical point is exceeded, emulsions of water-in-oil are formed.

Bhatnagar²³ believes that Robertson was able to emulsify 91.74 per cent olive oil in 9.26 per cent alkali, but the strength of the latter was almost 5*N*. He further observed that with decreasing strength of alkali the critical points were shifted toward the point of closest packing. If Robertson had used still weaker alkalies and stabilized his emulsions by following the precautions suggested by Donnan, adding the phases in small portions as advocated by Bancroft, it would have been possible for him to obtain a ratio of 74:26. Bhatnagar believes that the volume

Table 6
(Bhatnagar)

Alkali (cc)	Olive Oil* (cc)	Strength of Alkali (<i>N</i>)	Volume Ratio at Inversion Point
25	73.5	1/1000	74.0: 26.0
20	58.4	1/ 700	74.5: 25.5
25	72.7	1/ 500	74.4: 25.6
20	75.2	1/ 100	79.0: 21.0
10	88.9	1/ 50	89.0: 11.0

* Containing 0.5 per cent free oleic acid.

percentage of 74.048 holds only when the aqueous phase is very weakly alkaline 1/1000 to 1/500*N*). With alkalies of greater concentration, higher ratios are obtained, and Robertson's results can generally be duplicated. Emulsions prepared with concentrated alkalies break up, yielding a stable,

creamy substance having a volume ratio of 74:26. He also found that the phase ratios of alkali and oil at the critical (inversion) point, using alkalies varying in strength, were as recorded in Table 6.

The change in volume ratio with more concentrated alkali is due, according to Bhatnagar, to "the solid or gelatinous film" which envelopes the oil globules, thereby interfering with coalescence of the globules on touching one another. This investigator also showed that with very low concentrations of the emulsifying agent, the phase ratio alone determines the formation of one type of emulsion or another in the case of viscous oils, such as paraffin and olive oil, but not with light oils, like kerosene.

Emulsions of water in benzene between the approximate limits of 75 and 96 per cent water by volume were obtained by Newman¹⁸⁰ with his shaking machine. However, these limits were considered as having no theoretical significance and would probably be changed with a more perfect method of emulsification. Newman also indicated that no water-in-oil emulsions are formed when olive oil and water are shaken, using sodium oleate or caustic soda as an emulsifier. What Robertson thought was an emulsion of water-in-oil was actually only sodium oleate, or the sodium salt of other fatty acids suspended in oil. No emulsions of water in benzene were obtained with sodium oleate as emulsifying agent.

Emulsions made of toluene, benzene, and paraffin in a 0.4-per cent gelatin solution were prepared by Woodman,²⁸⁹ the percentage of oil to the total volume of both phases varying from 0.7 to 83.3 per cent. On standing, these emulsions "creamed," and an analysis of their cream showed it to be of fairly uniform composition, containing on the average 75 per cent of the internal phase.

According to Hatschek,¹¹⁵ emulsions containing a large percentage of the disperse phase (particles of microscopic or nearly microscopic size) are stable, or at least more than transient, only when the interfacial tension between the phases is low. Stability of emulsions, however, is again dependent on the phase ratio, and is generally not complete unless it approaches the figure corresponding to the closest packing. Also, the rate of separation into layers depends on the difference in the density of the phases, the viscosity of the continuous phase, and the degree of dispersion. Obviously, it is of interest to know that a system stable at all ratios is conceivable if both phases have the same density, *e.g.*, castor oil in water with alcohol.

Generally speaking, emulsions cannot be inverted by merely changing the volume ratio, as postulated by Ostwald. Usually, a given emulsifying agent will form an emulsion of only one type, regardless of the phase ratio. The effect of volume ratio on the stability of emulsions of Nujol, a highly-purified mineral oil, and two commercial lubricants, was studied by Parsons and Wilson,¹⁸⁰ using a dilute sodium oleate solution (0.033*M*) as emulsifying agent. The volume ratio of oil to water in these emulsions was varied, but the total volume was kept constant. These investigators

found that the critical values for Nujol* and the lubricants tested were somewhat higher than the 74 per cent representing the amount of the internal phase for close-packed spheres, explaining that the amount emulsified above that percentage was more or less a measure of the ability of the films to resist rupture when distorted beyond their normal spherical shape. Also, it indicated that the globules were not uniform in size after the critical point was reached, for the substances emulsified gave what appeared to be only a temporary water-in-oil emulsion. However, Parsons and Wilson state further that in general no true inversion was noted when the volume ratio alone was varied in the case of the three oils studied; but, as would be expected, there was a maximum amount of oil which could be stabilized by sodium oleate. Above this critical point, which was well-defined for each oil, breaking of the emulsion occurred.

Although globules of some petroleum emulsions appear to be nearly uniform in size when seen under a microscope, it is Wright's opinion^{29a} that in many cases the dispersed particles vary in size. Old emulsions, in particular, are characterized by globules which have departed widely from their spherical form enclosed by visible skin-like membranes. However, as ascertained by Berkman,²⁰ the size of globules in emulsions four to five years old naturally varies, but their shape in stable emulsions remains spherical. Actually, the shape of globules changes or is deformed only when an emulsion becomes unstable. In emulsions, the globules usually are not uniform, and there appears to be no reason why the ratio of the volume of the internal phase to the total volume of the emulsion should be of any particular magnitude. However, the actual ratios obtained do not differ markedly from those of uniform, close-packed spheres, being generally from 65 to 80 volumes for every 100 volumes of emulsion. These figures are independent of the proportions of the internal phase and the external phase at the beginning, so long as the former does not exceed 80 per cent.

Ostwald's assumption, as well as his formula for calculating the volume relation of emulsion phases, is logical and applicable insofar as it concerns theoretical emulsion systems. In actual emulsions, the volume relation cannot be considered as a characteristic determining the stability of an emulsion system. The volume ratio varies according to the system and probably indicates its equilibrium state. In other words, every system in time reaches a static equilibrium corresponding to a certain volume relation of the phases composing the system. But the absolute value of the equilibrium state, calculated theoretically by Ostwald for one system, assuming uniformity of the globules of the disperse phase in theoretical but not actual emulsions, is not applicable to any other system. On the basis of volume relation alone, the permanence of an emulsion system cannot be predicted, for the phase volume relation is one more factor to be taken into consideration when examining complex emulsion systems; it may be of help in determining the conditions for equilibrium in a permanent emulsion.

* Critical values for Nujol, 0.84 and 0.83; for the two lubricants, 0.87.

Electric Charge

When a liquid is dispersed in a liquid to form an emulsion, the particles of the disperse phase in most cases, if not in all, have been found to be electrically charged, that is, the particles are surrounded by a film which is negatively charged on one side and positively charged on the other side. The stability of the disperse phase is considered as being determined by the charged double-layer, and this arrangement constitutes a kind of spherical condenser, the thickness of which is small in comparison with its radius,^{3, 87a} the particles moving under an applied electromotive force, some going to the anode, others to the cathode. Under the influence of the electric field, this double-layer becomes distorted so that the positive charges accumulate on one side of the globule and the negative charges on the other.

It has been known for a long time that electrically charged films may function to prevent coalescence, because of the repulsion of like charges. The fact that there is movement of colloidal particles under electrical stress was recognized by Linder and Picton,¹⁵⁷ and this migration indicates the presence of charges of definite polarity on the particles themselves. In connection with the general theory of the protective action of the surface film, it is assumed that these electrically charged films are formed by the preferential adsorption of ions of an electrolyte (Freundlich). The fact that charged colloidal particles are discharged by solutions of electrolytes, because of the adsorption of an ion carrying a charge opposite to that already on the particles, is in accord with the theory of surface condensation of ions. Later, Linder and Picton showed that the precipitated material was contaminated by the electrolyte, and particularly by that ion of the electrolyte which, since its charge was opposite to that of the colloidal particle, functioned as an effective precipitating agent.

As shown by the work of several investigators, the rule of Coehn^{48, 49} that, for two phases in contact, the phase with the higher dielectric constant assumes the positive charge, holds true in some cases, but not in all. Since water has a higher dielectric constant than oil, according to Coehn's rule the oil globule suspended in water should be negatively charged, while water is positively charged. Ellis⁶⁵ found negative oil particles in dilute emulsions of cylinder oil and paraffin oil, and Mooney^{172, 173} observed the same charge relation in very dilute emulsions of highly refined Nujol and Stanolind.* Globules of the disperse phase of oil emulsions composed of linseed oil, wood oil, and fish oils, their compounds and polymers, used in the preparation of japan bases, are negatively charged, according to Davey.^{51, 52} He considered this fact a means of separating the disperse from the continuous phase, *i.e.*, by placing electrodes in the emulsions a deposition of the disperse phase on the anode takes place, the process being similar to electroplating. Davey found that the amount

* Both Nujol and Stanolind are commercial oils, the former consisting of saturated hydrocarbons of the paraffin series, while the latter is a paraffin hydrocarbon much like Nujol.

deposited is strictly proportional to the product of the current and the time and is independent of the voltage.

Sherrick²⁴⁴ found evidence in a West Texas petroleum emulsion that the oil is the continuous phase, the water being dispersed in it as negatively charged globules; this is not in agreement with Coehn's rule. It has been suggested by Gurwitsch⁹² that this anomaly may be due to the fact that the charge is carried by the resinous films surrounding the oil globules rather than by the oil itself. In discussing Coehn's rule, Briggs³² pointed out that glass, which should have been negatively charged against glacial acetic acid, was positively charged after long standing in this acid, the same holding true for propionic acid. In the case of xylene, toluene, and other liquids in which the dielectric constant is small, electric endosmosis takes place so slowly as to be negligible. By adding a trace of hydrochloric acid to improve conductivity, electric endosmosis occurred, and the glass became positively charged against the medium used. Acid added to other liquids made the glass less negative. According to Briggs, the question arises as to whether the positive charge on the glass, when in contact with xylene or toluene, may be due not to the hydrochloric acid present, but to the small dielectric constants of these liquids. This point should be proved experimentally. It is evident that the cases referred to by Briggs contradict the rule of Coehn; but, on the other hand, no parallel can be drawn between the cases mentioned and the systems herein discussed, because Briggs refers to a solid/liquid system and this case concerns emulsions which are liquid/liquid systems. In general, Coehn's rule may be applicable to two-component emulsion systems; but, when an emulsifier is added, conditions change and the relationship becomes more complex.

McBain¹⁶⁴ explains the origin of the charge on the dispersed globules of an emulsion system by the presence of ions. His hypothesis is based on an exhaustive experimental study of the behavior of soaps in solution, according to which particles are charged by the adsorption of molecules of an electrolyte, which is consequently dissociated to some extent, giving rise to a small portion of ions, possessing the same freedom and mobility as in an ordinary aqueous solution of an electrolyte, and remaining fixed on the dispersed particles. Urban and White²⁶⁸ are of the opinion that the presence of an electric charge on the dispersed particles of an emulsion has been proved for many systems, and should be considered an important factor in the stabilization of emulsions.

Mukherjee¹⁷⁵ stated that the origin of the charge on a colloidal particle is believed to be due to the adsorption of ions. In his theory of adsorption, Langmuir¹⁴² refers it to "chemical forces" caused by surface atoms. The adsorption of an ion charges the surface and as a result introduces electrical forces. The recognition of this fact throws light on the influence of electrolytes, on the precipitation of suspensoids, on electric endosmosis, and on related phenomena. A certain number of "chemically adsorbed" ions are covered by ions of an opposite charge, depending on the concentration of the oppositely charged ions in the liquid near the surface at

any moment, the total number of ions of opposite sign, both bound and free, being equivalent to the number of ions chemically adsorbed. A number of free ions, equal in number to the "chemically adsorbed" ions on the surface, are present at the liquid interface, and these free ions form the second layer of the double layer. Langmuir is of the opinion that, as a result of their thermal motion, the mean distance between the two layers is greater than the molecular dimensions.

According to Michaelis,¹⁶⁹ the charge on a suspended particle may originate in one of two ways: (1) through so-called "oppositional adsorption," *i.e.*, when the surface of the globule exhibits chemical affinity for certain ions, and (2) by dissociation of the globule substance or the emulsifying agent, *i.e.*, when the anion resulting from the ionization of a molecule adsorbed on or dissolved in a globule gives to the molecule a negative charge. If the emulsifying agent is a protein, loss of hydrogen ions from the carboxyl groups would render the phase in which it originated more negative, while the addition of hydrogen ions to an amino group results in a positive charge. The charge may also be developed by the adsorption of ions without any chemical activity on the part of the emulsifying agent or the substance of the globules. This assumption is based on the fact that the adsorption of ions bearing the effective charge is responsible for the stability of the emulsion and the electrokinetic behavior of the particles.

In a three-component emulsion system, the particles of the disperse phase carry an electric charge, and when current is passed through, cataphoresis takes place. The rate at which oil rises through the continuous phase is dependent upon its specific gravity, the viscosity of the continuous phase, and the size of particle. The velocity V , through which the particle rises, may be expressed by the equation:

$$V = \frac{2r^2(S - S')}{9\eta} g$$

where r is the radius of the particle; $S - S'$, the difference in specific gravities of the two liquids; g , the gravitation constant, and η , the viscosity of the continuous phase.

Lamb¹⁴⁰ and Smoluchowski^{254, 255} considered the charge on the colloidal particles to be due to associated ions, which account for ionic migration, diffusion and permanent suspension of the emulsion particles. According to Smoluchowski, the electric properties of an emulsion are not to be attributed to the charged particles alone, but to the fact that the adsorbed ions of opposite sign collect in the continuous phase about each droplet and form a double sphere of charges termed the Helmholtz double-layer. The outer sphere of the double-layer was first thought to be close to the suspended particles, and of molecular dimensions. Burton,³⁸ and many others, however, believe the outer layer to be a diffuse arrangement of ions, which Burton calls an "ionic atmosphere." McBain and Usher assumed that very few ions in a double-layer are mobile, most of them being immobile. Gouy^{85, 86, 87} postulated a diffuse

double-layer, the outer ionic layer possessing an electric density falling off according to an exponential law, all its ions participating in cataphoretic movement. Milner,¹⁷¹ and also Debye and Hückel,⁵³ extended the work of Gouy and showed that an ion in a solution must be accompanied by an oppositely charged "ion atmosphere," which is the balanced result of the electrostatic forces (attractions and repulsions) tending to ordered array of the ions and the thermal vibrations acting against such an arrangement. Taggart²⁶⁴ made known the relation between electric charge, pH, and Brownian movement.

Concerning the many explanations offered by different investigators, of the origin of the electric charge all contain some truth, but none, except Stern's theory²⁶⁰ of the double-layer (a monomolecular film adhering to the boundary), can be accented as a working hypothesis for all kinds of emulsion systems. In his theory, Stern resolves Gouy's double-layer into a rigid monomolecular layer of the Langmuir type, and a diffuse outer layer, the double-layer being regarded as a condenser, one side of which is the interface having a homogeneously distributed charge. On the liquid side of the interface the electric charge is concentrated partially in the surface and partially in the electrolyte, the density of the charge decreasing asymptotically toward zero.

The names of several investigators who determined the total charge on particles, as well as the potential difference existing between each globule of the disperse phase and the liquid medium surrounding it, are mentioned in the literature on emulsions. It has been pointed out by Lewis^{154, 154a} that one of the most characteristic properties of emulsions is the ability of their particles to show movement in one direction or another when the solution is in contact with an electric field. This would indicate the actual presence of an electric charge, e , on the oil globules, which may be determined by Stokes' equation, namely:

$$e = \frac{6\pi\eta rV}{x}$$

where V is the velocity; r , the radius of a particle moving through a liquid medium whose viscosity is η ; and x , the potential gradient units per cm, found to be equal to 4.4×10^{-7} electrostatic unit. Stokes' equation considers the globule with its electric double-layer as a small condenser composed of two concentric rings, the distance between which is small compared with the radius of the globule. Lewis assumed that the value of the charge on an emulsion particle was of the same order of magnitude as that of Burton's colloidal metals, indicating that oil-in-water emulsions resemble colloidal metals, and perhaps are subjected to the same conditions inducing equilibrium. Ellis⁶⁵ found the charge on an oil droplet in a very dilute emulsion to be about 2.05×10^{-6} electrostatic unit.

Variations in cataphoretic mobility of oil globules in water were investigated by Mooney,^{172, 173} who found that very dilute emulsions of bromoform, bromnaphthalene, dimethyl aniline, iodobenzene, phenetol, phenyl mustard oil, tribromhydrine, *m*-xylene, Nujol and Stanolind

could be prepared in water. In all cases, the oil globules were negatively charged. Mooney indicated that the mobility for a field of 10 volts/cm, even in pure water, increased with an increase in the diameter of the globules, that is, between 0.0005 and 0.04 mm; and, as the diameter increased, the mobility asymptotically approached an upper limit. From the curves obtained by Mooney, it cannot be definitely ascertained whether the lower limit, D , approaching zero, is zero or finite. Mooney also proved that Smoluchowski's theory, according to which cataphoretic mobility is independent of the external field, holds true only for small globules below 0.02 mm in diameter. Usher predicted a relationship between mobility and size of dispersed particles, basing his prediction on the surface dissociation theory of the electric double-layer. It is Abramson's opinion² that there is no correlation between particle size and cataphoretic mobility. Roberts'²²⁴ experiments showed a reversal in the direction of cataphoretic movement in old emulsions, new emulsions possessing strong cataphoresis which gradually became weaker, ceased entirely for a time, and then changed into weak anaphoresis, this cycle being completed in eight weeks.

Taking into consideration the suggestions first offered by Lamb, and eventually incorporated into Helmholtz's double-layer theory, the potential difference between the oil globules and the continuous phase of an emulsion may be calculated from the migration velocity of the disperse phase, having a known potential gradient. The potential difference between particles and medium of metal sols was determined by Burton, using Lamb's modified equation:

$$V = \frac{4\pi\eta V_1}{K \cdot X}$$

where K is the dielectric constant of the medium; η , the viscosity of the medium; and V_1 , the migration velocity of the particles in cm/sec, having a potential gradient of X units per cm. Lewis¹⁵¹ found that the potential difference between oil globules and water is 0.05. The fact that the values for the potential difference of the particles are all of about the same order of magnitude is considered by Lewis as very important. However, any specific effect due to the chemical composition of the disperse phase is not evident. Further, investigations of Lewis showed that the potential difference of particles in his emulsion systems is independent of the chemical nature of either the disperse phase or the dispersion medium. Regarding the mechanism by which the potential difference is set up, Lewis assumed two factors as important, namely, the effect of the electrolytic ion and the electronic effect. As regards the first, it is evident that different electrolytic ions come into play with a change in the dispersion medium. The chief objection to this point of view is that emulsion systems can be prepared in which electrolytic ions are not likely to be present. The electronic viewpoint appears to be applicable in all cases, and the absence of any specific effect due to the chemical composition of the disperse phase, as noted above, is very strong evidence in its favor.

According to Freundlich and Rona,⁷⁹ there are two kinds of potential. The electrokinetic potential is measured by cataphoresis and electro-endosmosis; it is less than the static boundary potential. The potential difference between the interior of the glass and the liquid on the outside is ϵ , electrostatic potential. The electrokinetic potential is determined by measuring the streaming potential in a capillary tube according to the formula:

$$\zeta = \frac{4\pi\eta U}{HD}$$

in which D is the dielectric constant of the dispersion medium; H , the potential gradient in volts/cm; and U , the cataphoretic migration velocity. The electrostatic potential is little affected by the presence of ions, while the electrokinetic potential varies greatly with the kind and quantity of ions present. The valence of the ion has no influence on the electrostatic potential, but is important in the electrokinetic potential. The electrokinetic potential is actually a measure of the difference in potential between the mobile and the immobile portions of the liquid, while the electrostatic potential measures the total difference in potential between the solid wall and the liquid. The stability of colloids is governed by the electrokinetic potential, not by the electrostatic potential. This indicates an ionic source of charge, particularly since the sign of the charge may be reversed by the addition of certain ions. Freundlich and Elisafoff⁷⁸ pointed out that the particles of the disperse phase may give rise to ions participating in the formation of the electric double-layer. In the case of ionogenic substances, such as metal hydroxides and sulfides, this idea holds true; with typical co-valent compounds, such as naphthalene, it is not applicable. In such cases, the charge has been ascribed to other causes.

Table 7

(Ellis)

Hydrocarbon	Electrokinetic Potential (volt)
Special acid-free oil	0.050
Acid-free oil	0.045
Pure liquid paraffin (Kuhlbaum)	0.040
Cylinder oil	0.050
Water-soluble oil	0.066

In most cases, emulsion systems not only consist of two immiscible liquids, but also contain electrolytes, which may affect the difference in potential between the pure dispersed oil and the pure liquid medium in which it is dispersed. The potential of the emulsion systems which Ellis^{65, 66} investigated was not greatly affected by organic impurities, such as wool grease in oils, but was very sensitive to small proportions of electrolytes. By using highly refined hydrocarbon oils in the preparation of dilute emulsions, he obtained the values for electrokinetic potential listed in Table 7.

Table 8. Migration Velocity of Emulsions of Acid-free Cylinder Oil
(acid as oleic acid and less than 0.3%)
in the Presence of HCl and NaOH.

Electrolyte Solution	Electrokinetic Potential at Oil/Water Interface (volt)
1/10 <i>N</i> HCl	0.0
1/40 <i>N</i> HCl	0.0022
1/100 <i>N</i> HCl	0.0088
1/200 <i>N</i> HCl	0.0185
Neutral	0.050
1/1000 <i>N</i> NaOH	0.072
1/500 <i>N</i> NaOH	0.068
1/100 <i>N</i> NaOH	0.042
1/20 <i>N</i> NaOH	0.022

Ellis also determined the effect of acids and alkalies, and found their influence on the difference in electrokinetic potential at the oil/water interface as shown in Table 8.

The results obtained show that the electrokinetic potential at the oil/water interface reaches a maximum in either a neutral or a slightly alkaline solution. The addition of hydrochloric acid diminishes the electrokinetic potential very quickly for small concentrations, and slowly for relatively high concentrations. The addition of sodium hydroxide first increases the electrokinetic potential at the oil/water interface, but when the concentration exceeds 0.01*N* sodium hydroxide, the potential drops quickly at first, and then more slowly. The electrokinetic potential at the oil/water interface varies for different oils, depending on the amount of impurities present. The electrokinetic potential in a neutral solution is dependent on the dielectric constant of the suspended particles and the medium in which they are suspended. Ellis interpreted the decrease in the potential by addition of hydrochloric acid and sodium hydroxide as the beginning of electric adsorption.

Powis^{203,204,205} makes clear the influence of different electrolytes applied in varying proportions upon the difference in potential existing at the interface of cylinder oil-in-water emulsions. He found, for instance, that small percentages of potassium chloride, up to 2.5 millimols/liter, increased the negative value, whereas larger proportions decreased it. All anions in an aqueous solution have a tendency to make the potential difference negative, and cations tend to make it positive. In pure water and at low concentrations, the negative influence is greater. The influence of both cations and anions increases with an increase in their valence, the higher the valence of the cation the more effective the salt in reducing the potential. Powis correlated his results with the viewpoint of Freundlich,⁷⁷ who believed that the effect of electrolytes on the potential is due to the preferential adsorption of ions. The influence of potassium chloride, barium chloride, aluminum chloride and thorium chloride on the potential at the glass/water interface is similar to that at the oil/water interface, except that addition of small percentages of potassium chloride and potassium ferrocyanide increases the negative value of the charge of the water. The lower the concentration of the oil particles, the lower the

concentration of the electrolyte required to bring about a given potential difference.

Gyemant⁹³ studied the influence of electrolytes on the cataphoretic mobility of water-in-oil emulsions, using guaiacol and aniline. Water or solutions of inorganic electrolytes showed very little, if any, migration. Cataphoresis was found to be favored by those electrolytes which easily infiltrate into the organic solvent. In the presence of organic cations, water globules migrate to the anode and organic anions to the cathode. Benzonitrile gave unexpected results, possibly due to impurities, *e.g.*, benzoate anions.

Millikan¹⁷⁰ investigated the specific inductive capacity of emulsions composed of water dispersed in a benzene/chloroform mixture. Considering water globules as conductors and the organic phase as the insulator, he applied the Clausius-Mosotti equation:

$$k = K' \frac{1 + 2x}{1 - x}$$

where k is the dielectric constant of the emulsion; K' , the constant of the organic phase; and x , the ratio of the volume of the disperse phase to the total volume of the emulsion; he obtained a good agreement between the results calculated and those observed.

Sen²³⁸ estimated the potential drop between two phases by experiments with cataphoresis and electro-endosmosis. Since the potential drop between oil and water is negative, the presence of potassium chloride and potassium ferrocyanide concentrates more negative ions in the oil interface, so that a greater negative charge is built up. Potassium ferrocyanide raises the negative charge more than potassium chloride. In the case of mixtures of potassium chloride and barium chloride or potassium ferrocyanide and barium chloride, there is considerable antagonistic action, because one of these electrolytes raises the value of the potential drop, while barium chloride lowers it. When using a mixture of potassium chloride and potassium ferrocyanide, only a slight antagonism results, because at certain concentrations potassium chloride causes a decrease, while potassium ferrocyanide still raises the negative charge. However, the effect is not so pronounced as with barium chloride.

Limburg,¹⁵⁶ in connection with the theories of Freundlich, Smoluchowski and Gouy, dealt with the influence of the electric charge of the particles and the adsorption surfaces on the critical mobility of the particles, the speed of coagulation of emulsions, and the influence of electrolytes [KCl, K₂CO₃, HCl, BaCl₂, AlCl₃, and Th (NO₃)₄] on the cataphoretic mobility of an emulsion of paraffin oil in water. On addition of potassium chloride and hydrochloric acid, the cataphoretic mobility was found to pass through a maximum with increasing electrolyte concentration. With potassium carbonate the maximum was not reached, but the increase in cataphoretic mobility at low concentrations was relatively high. A decrease in mobility of the particles following the maximum, in

the case of addition of hydrochloric acid and potassium chloride, has been explained by the fact that the tangential potential difference becomes smaller with increase in electrolyte concentration. Barium chloride does not influence the cataphoretic mobility at fairly low concentrations. Aluminum chloride and thorium nitrate cause a change in the charge on the particles, probably by covering them with products of hydrolysis; when hydrolysis was prevented, no change in charge occurred with aluminum chloride.

Electrolytes added to, or present in, an emulsion system which already contains an emulsifying agent, influence emulsification in the same manner as the potential difference at the oil/water interface. Donnan⁵⁴ confirmed the effects produced by alkalies and salts on the potential difference at the interface of a neutral emulsion of hydrocarbon oil and water, emulsified by means of sodium oleate. Hatschek¹¹⁴ approached the question of the action of electrolytes in an emulsion system from the standpoint of electric discharge, differentiating two steps in the discharge effect: (1) the discharge of the emulsion particles by cations occurs when a sufficient percentage of electrolyte is present; and (2) the discharged particles exhibit Brownian movement, and there is no repulsion between them—only collision and a coalescence to form larger particles. This process continues, but with decreasing speed because, as the size of the particles increases, their movement is retarded until a limit is reached at which Brownian movement apparently ceases. This limit depends, of course, on the mass and also on the difference in specific gravity between the disperse phase and the continuous phase, as well as on the viscosity of the latter. If no great difference in specific gravity exists between the phases, only a change in the degree of dispersion can take place after discharge by electrolytes, *i.e.*, precipitation cannot occur.

In discussing the fact that, in general, an electric double-layer existing at the interface and separating two phases gives rise to a number of important phenomena due to the adsorption of ions from solutions of electrolytes, Shorter^{246, 247} states that the principal factors regarding the effect of electrolytes may be summarized as follows: (1) the effect of a given number of ionic charges increases with an increase in the valence of the ions on which they are located; (2) in dilute solutions, both the hydrogen ions and the hydroxyl ions produce an abnormally strong effect; and (3) the ion having a charge opposite to that on the surface has a greater tendency to be adsorbed than one of like charge. The technical importance of the surface charge lies in the fact that such charges affect the stability of fine suspensions and emulsions. Bases in dilute solutions tend to stabilize, whereas acids exert a coagulating effect. In the case of positively charged particles, hydroxyl ions coagulate and hydrogen ions stabilize. In more concentrated solutions, the specific activity of the hydrogen ions and the hydroxyl ions disappears, and the ion with a charge opposite to that of the particle is adsorbed, decreasing the charge. As both positive and negative ions are always present in equivalent amounts, the ionic species present must be considered.

Pickara,^{196, 197, 198} in his article, "On the Dependence of the Dielectric Constant of an Emulsion on the Volume Concentration of the Dispersed Phase and on the Degree of Dispersion," states that on the basis of his investigation three secondary electrical phenomena, caused by the charge on the globules, are possible. (1) The vibrations of the charged particles are synchronous with the external alternating field, except in the case of those emulsions in which the mass is large and the movement slow; for example, Vaseline emulsions have a high internal friction, so that little movement is possible. (2) A double-layer is formed around each globule of the emulsion, and the dielectric constant is not influenced. (3) In liquid emulsions, the electric charge exerts a directing influence on the dipoles surrounding the globule, thereby decreasing the dielectric constant of the emulsion, because the directed dipoles do not participate in the polarization of the dielectric and are not at all affected by the vibrations of the external field. In oil emulsions at constant volume concentration, the dipole effect increases with the number of globules present. The decrease in the dielectric constant of water-in-oil emulsions is small, about the order of magnitude of 10^{-3} . In colloidal solutions where the dispersion medium is water with a marked dipole character and a high degree of dispersion, the dipole effect is much stronger. The actual dielectric constants are much higher than those calculated according to one of many formulas derived to express the dielectric constant of a mixture as an additive function of the dielectric constants of the constituents; for instance, the general formula of Lorenz.

$$f(\epsilon) = \frac{\epsilon_1 - 1}{\epsilon_1 + 2}$$

where ϵ is the dielectric constant of the mixture and ϵ_1 and ϵ_2 , the dielectric constants of the two constituents of the system.

Pickara,¹⁹⁸ in studying the dielectric constant of emulsions of mercury in Vaseline and oil, applied the Lorenz-Lorentz formula:

$$\frac{\epsilon - 1}{\epsilon + 2} = \delta \frac{\epsilon_1 - 1}{\epsilon_1 + 2} + (1 - \delta) \frac{\epsilon_2 - 1}{\epsilon_2 + 2}$$

in which ϵ is the dielectric constant of the mixture; ϵ_1 and ϵ_2 , the dielectric constant, DK , of both substances, and δ , the volume concentration of the constituents. Other formulas of Beer, Silberstein, Wiener and Lichte-necker are not applicable because they give an infinite value for ϵ in this case. For emulsions of alcohol-water mixture and mercury in paraffin oil, the dependence of ϵ on δ (for $\delta < 0.002$) is very close to linearity; on the contrary, for emulsions of mercury in Vaseline, this dependence is absolutely linear (even for $\delta < 0.034$). As the reason for the deviation from linearity for liquid emulsions, Pickara assumes a directing action which the electric charge of the globules exercises upon the dipole molecules of the liquid. The directed dipoles react very little upon the vibrations of the external field, and in such a manner that the dielectric constant

of the emulsion is decreased. These secondary phenomena do not occur in Vaseline emulsions; consequently Pickara assumes that, for ideal mixtures of very small volume concentration of the continuous phase (closed phase), ($\delta < 1$), ϵ is a linear function of δ .

The electric charge carried by the globules in an emulsion and the potential difference between the dispersed globules and the dispersion medium are related directly to the stability of an emulsion system. Rabinerson and Kremnev²¹⁰ group emulsions into three classes: (1) dilute emulsions stabilized by the electrokinetic charges; (2) concentrated liquid emulsions stabilized by protective films, or emulsifiers; and (3) foam-like emulsions stabilized by the mechanical rigidity of the lamella. These emulsions in turn are classified according to their composition, namely, water-in-oil and oil-in-water, etc.

Ellis,^{67,68} in his article, "The Stability of Emulsions and Size of Globules," states that the stability of a pure water-in-oil emulsion is greatest when the electrokinetic potential reaches a maximum, *i.e.*, in dilute alkaline solutions. When an acid or an alkali is added to solutions of concentrations greater than 0.001*N*, the stability of an emulsion is decreased by an amount corresponding to a decrease in the electrokinetic potential. He also states that the stability of a pure water-in-oil emulsion depends very much on the electrokinetic potential at the oil/water interface, but does not depend on the surface tension. A decrease in stability with a decrease in electrokinetic potential is explained by a decrease in the strength of the electric double-layer; the latter can be very readily destroyed, enabling the emulsion globules to coalesce. When the electrokinetic potential reaches zero, the stability becomes zero, and coagulation takes place with the greatest rapidity. Ellis, discussing the relation between coagulation and electrokinetic potential, points out that the total coagulation produced by means of a colloidal ferric hydroxide solution in an oil-in-water system takes place at a definite electrokinetic potential, *i.e.*, between 0.045 and 0.03 volt.

The results of Powis²⁰⁵ on the stability of emulsions with regard to the electric charge of the disperse phase indicate that if the potential difference of an oil-in-water emulsion exceeds a certain critical value, which is about 0.03 volt (either positive or negative), the emulsion is relatively stable. If the potential difference at the oil/water interface is not large enough, coagulation of the suspended oil droplets occurs with a speed that is about the same for all values of the potential. Such behavior is not in accordance with the assumption of Ellis, *i.e.*, that stability decreases continuously with the potential, becoming very small at the iso-electric point. The relative concentrations of electrolytes, such as thorium chloride, aluminum chloride, barium chloride, potassium chloride, and others, which are necessary to obtain a potential of 0.03 volt, are nearer to those which cause rapid coagulation than to those which reduce the potential to zero. If coagulation does take place, the particles clump together rather than coalesce. The theory of a critical potential, above which an emulsion is stable and below which it is unstable (as believed

by Powis), agrees with most of the known facts on the stability of colloidal solutions, and explains many facts which are not in agreement with the theory of the iso-electric point.

It has been thought by Willows²⁸⁵ that rapid coagulation depends wholly on the rate of diffusion. From a comparison of the results obtained by Willows, using varying proportions of electrolytes, with those of Galecki,⁸¹ in which the relative charges on the sol were particularly measured, it has been concluded that rapid coagulation occurs before the iso-electric point is reached. This is in agreement with Powis' results on emulsions. However, whereas Powis found it sufficient to reduce the potential difference across the electric double-layer from 0.04 to 0.03 volt to initiate coagulation, Smoluchowski assumed that particles are attracted by "capillary" forces (nature not specified) when they approach one another, but that coalescence is normally prevented by the electric double-layer. When electrolytes are added, this layer is wholly or partially destroyed by ionic adsorption (mechanism not given). Brownian movement, on the other hand, tends to bring particles into contact with one another and, according to Smoluchowski, whenever the distance between the centers of two droplets becomes less than the radius R , coalescence occurs.

Willows, criticizing Smoluchowski's work, contends that it is entirely statistical. Smoluchowski does not attempt to account for the electric double-layer, the adsorption of ions, or the apparent attraction between particles. A complete theory, according to Willows, must explain the origin of the charge on the particles and show in what way the discharging ions penetrate the electric double-layer against the repulsion of its outer half. Two facts appear to be fairly well established, namely, that the final stability of emulsions depends only on the potential difference across the electric double-layer, as shown by Powis; contrary to Bredig's theory, Ellis finds no relation between surface tension and coagulation of emulsions.

Limburg's calculations,¹⁵⁶ in connection with Smoluchowski's theory, show that at high concentrations of hydrochloric acid the rate of coagulation has the greatest value theoretically possible, and therefore is independent of further additions of acid. In case aluminum chloride and thorium nitrate are added to increase the electrolyte concentration, first a stage of stability is attained, then one of precipitation, and finally stability again. High concentrations of thorium nitrate decrease the stability. In the case of aluminum chloride, the stability is increased considerably, to a point where the charge no longer changes. The stability curve of an emulsion at rest in the presence of potassium chloride is at first below the curve for a rotated emulsion, but above it at higher concentrations of the salt. According to Limburg, the relation between stability and electric charge indicates neither proportionality nor the presence of a critical potential, and assumes that the increase in conductivity is probably the most important factor in determining the stability of an emulsion. He also observed the changes in the cataphoretic

velocity of a paraffin oil-in-water system in the presence of protective colloids, and found that the addition of gelatin influences it, depending on the acidity of the emulsion. Higher concentrations of gelatin (pH 4.7) result in a cataphoretic velocity of zero, as is found in pure gelatin, because every oil particle is surrounded by a film of gelatin, forming a water/gelatin interface. The stability curves also show a minimum, depending on the acidity of the emulsion (the higher the pH, the lower the minimum stability). This is true of the concentration of the gelatin at which the charge becomes zero, so that the instability of the emulsion may be referred to as a discharge.

Steik,²⁵⁹ discussing oil-in-water and water-in-oil emulsions and types of stabilizers, states that electrolytes aid greatly in stabilizing emulsions; that a difference of potential exists between the disperse phase and the continuous phase, and that a difference of about 0.06 volt affords a fairly stable emulsion. When the difference of potential is zero, the emulsion breaks; this is the iso-electric point. The critical potential is considered to be a point which lies just above the iso-electric point, and at which the emulsion begins to break.

It has been explained by Brooks and Bacon³⁰ that the action of electrolytes in reducing emulsion stability and inducing coagulation may be considered as due (1) to the suppression of the diffusion of the outer layer of the Helmholtz electric double-layer, thereby reducing the effective distance at which the repulsive force between particles comes into play, and (2) to the actual discharge of the charged particles.

Donnan ascribes the high stability often shown by dilute emulsions, produced by shaking a pure hydrocarbon oil with distilled water in a silica container, to the influence of an electric double-layer which retards coalescence.

Usher²⁷¹ determined the total charge on the particles of a suspension by neutralizing it with a measured quantity of oppositely charged ions, and by the effect of electrolytes in modifying the surface charge. Ions which attach themselves to the spherical particles of a uniform, stable suspension of gamboge, during the process of neutralizing flocculating ions, displace ions originally attached to the particles, but do not contribute to their effective charge. The total charge on the flocculating ions is, therefore, greatly in excess of the effective charge considered responsible for the stability of the emulsion and for the electrokinetic behavior of the particles. When a suspension is diluted, an increase in the number of ions attached to each particle in the course of flocculation indicates that the net charge of the particles increases with their mean distance of separation. Among ions of the same valence, the flocculating power is determined by the solubility product of the compounds formed from both the flocculating ions and the stabilizing ions, the flocculating ions of the different electrolytes reducing the concentration of the ions stabilizing the suspension. Usher considers a theory involving slight dissociation of a layer of surface molecules preferable to other current theories in accounting for the results of experiments on mobility made in conjunction with

those on flocculation, and for the effect of dilution in increasing the stability of aqueous suspensions.

Roberts,²²⁴ in his theory of emulsions, emphasizes the fact that electrokinetic potentials and surface tensions exist on both sides of the interface, this conception being supported by interfacial tension measurements according to Harkins' ring method. Further, he assumes that an emulsion is stable only when the surface energy of the disperse phase is greater than that of the continuous phase for, from each phase, those molecules which decrease the difference in energy are shifted toward the boundary; for example, from the disperse phase, particles with the lowest polarity and from the continuous phase, particles with the highest polarity. Ions of high polarity tend to accumulate at the interface on the oil side, while ions of low polarity tend to accumulate on the water side. In the case of two antagonistic emulsifiers, such as sodium oleate and calcium oleate, a competition for position across the interface exists between them: calcium oleate in the oil tends to adsorb on the oil side, its polar end passing into the water, while sodium oleate in the water tends to adsorb on the water side, its non-polar end passing into the oil. The competition for position across the interface may result in a repulsion between adsorbed ions of like charge, and this will tend to reduce emulsion stability.

It follows from investigations on the electric charge and from attempts to explain the origin of the charge that: (1) the existence of an electric charge on the dispersed droplets of an emulsion is fully proved for many emulsion systems; and (2) the electric charge present on the dispersed droplets, analogous to other colloidal systems, must be considered as an important factor in the stability of emulsions. As for the various explanations given by different workers for the origin of the electric charge, all have a grain of truth, but not a single one, except perhaps the Helmholtz double-layer theory, can be accepted as a working hypothesis for all kinds of emulsion systems. That electric charges at interfaces, whatever their origin, contribute to the stability of emulsions has been an accepted fact for many years.

Size of Particles of the Disperse Phase and the Distribution of Sizes in an Emulsion System as Factors Relating to the Stability of Emulsions

Donnan,^{55, 56, 57} investigating the stability of colloidal solutions and emulsions in relation to surface tension, predicted a critical diameter when one phase is finely divided and completely dispersed in the other, basing his prediction on thermodynamic principles. The order of magnitude anticipated was 10^{-5} cm. Meunier and Maury¹⁶⁸ found that the radii of droplets of a mastic emulsion are equal to 0.52 to 0.56 μ , and of gamboge (gum resin) emulsions, 0.14 to 0.46 μ . Lewis¹⁵¹ proved the existence of the Donnan critical or equilibrium size of globules in a number of oil-in-water emulsions. He obtained an emulsion (2 per cent maximum oil content) in which the dispersed oil globules had a diameter of 4×10^{-5} cm, a value of the same order of magnitude as Burton^{40, 41} found for col-

loidal metals. Likewise, Lewis prepared an unstable emulsion of aniline in water, the globules of which also had diameters of the order 10^{-5} cm. While Lewis found 10^{-5} cm to be the order of the diameters of his emulsion particles, Ellis,⁶⁶ using similar emulsions prepared by shaking a special acid-free cylinder oil with water for two or three days, obtained globules of the order of 2×10^{-4} cm. Powis²⁰⁵ states that in his emulsions few globules exceeded 3×10^{-4} cm, or were less than 0.5×10^{-4} cm. Rubber latex emulsions examined by Henri¹¹⁸ contained 50 per cent of 2μ -diameter particles, the remainder being 0.5μ in diameter.

Roon and Oesper²²⁸ prepared emulsions of cottonseed oil, benzene, paraffin, carbon tetrachloride and chloroform in dilute soap solutions having globules of about 1 to 2μ in diameter. If gum acacia solutions are substituted for soap solutions, larger globules result, the diameters being from 3 to 50μ . Fischer and Harkins⁷⁴ measured the distribution of sizes for globules of paraffin oil (Finöl) in water with sodium oleate as emulsifier and found that the highest percentage consists of globules of the order of one micron. For benzene-in-water emulsions, using the same emulsifier, a slightly smaller globule diameter is more frequent.

Young^{294, 295} gives an example of spontaneous formation of an ordinary emulsion by mixing water, petroleum oil and an "automatic" emulsifier called "cresoap" (a mixture of soft soap and cresol). The author compares this emulsion, which acts as if it were alive, with living protoplasm, because of the flowing and revolving movements which it exhibits. Schemyakin²³² succeeded in producing a multiple macro-emulsion (toluene/gelatin/water). Its formation is spontaneous, and it consists of a suspension of gelatin globules (diameter 0.1 to 0.25 cm) containing minute droplets of toluene which float in the excess toluene; it resembles frog eggs in appearance. In case of diffusion of alkali in gelatin and agar-agar gels, replaced by chlorhydrate, spontaneous formation of a chloroform emulsion was observed. Kniga and Wischnewskaja¹³⁵ stated that a double emulsion (the emulsion drop of the external emulsion contains still smaller drops of the internal emulsion) is obtained when benzene and water are emulsified with lecithin.

The actual size of the particles was determined by different investigators for various emulsion systems, but the particle sizes of the disperse phase cannot be averaged in this manner. In order to ascribe a certain order of magnitude of size to the disperse globules, the distribution of sizes in the emulsion investigated should actually be obtained.

The particle size of the disperse phase may be an important factor in determining the type, amount, and permanence of an emulsion system. All emulsions contain globules of different sizes, and it is only possible to estimate very roughly what the average size may be. In semi-solid emulsions the globules are much smaller than in ordinary liquid emulsions. When an oil is emulsified in a soap solution to form a durably stable emulsion, there is a dominant size of about 1.0 to 1.5 microns in diameter; but there are some globules three or four times this size, as well as much larger ones of 25 to 30 microns, or smaller ones, down to

one-tenth of the dominant size. The character of the oil has an effect on the size of the globules. Emulsions of the lighter paraffins, such as the various naphthas and gasoline, are fairly fine-grained. Crude petroleum contains heavy hydrocarbons, such as lubricating oils, asphalt, asphaltenes, and usually small proportions of earthy material, which are probably present in colloidal solution and may be reasonably expected to act as emulsifying agents. The nature of these asphalt-like bodies in the crude oil probably depends on the ratio of the light fractions to the lubricating fractions; and consequently the tendency to emulsify should be expected to vary, the tendency toward emulsification decreasing as the dispersion approaches a true solution. This indicates that the degree of dispersion of the asphalt-like bodies is more favorable for emulsification in light fractions than in heavy ones. (The effectiveness of asphalt as an emulsifying agent was tested by Dodd in preparing emulsions of distilled water dispersed in gasoline solutions of asphalt at various concentrations).

Wright^{293a} states that it has been found from a study of oil-field emulsions that their age can be determined approximately by microscopic examination of the disperse phase. For example, when the globules are spherical in shape but vary greatly in size, it is safe to assume that the emulsion is of recent origin and formed at, or near the point of, production. When the globules are spherical in shape and uniform in size, it may be assumed that the emulsion was formed sometime prior to, and not at the point of, production. Finally, when the globules are irregular in shape, but of uniform size, with a withered, skin-like membrane surrounding them, somewhat like linsced oil which has been dried in air, it is safe to assume that the emulsion is very old, probably due to the admission of water to the oil under pressure in years past.

Wiegner,^{282, 283, 284} discussing the phenomenon of "hysteresis" in emulsion systems, indicated that an emulsion changes the number of its particles until it reaches a final stable state, the alteration depending upon the preparation, or on the so-called "prehistory" of the emulsion.

By using a de Laval centrifuge for the preparation of a very fine dispersion of olive oil in water, from 1 cc 5×10^9 oil globules could be centrifuged. Wiegner assumed that olive oil is so finely divided in water that the disperse phase can no longer be separated by the action of specific gravity and the system acquires colloidal properties. Pickering's hypothesis¹⁹⁵ on emulsification has as its principle films of insoluble particles enveloping oil globules. He expressed the opinion that emulsification depends solely on the size of the dispersed particles forming the precipitate, and that the average size of the globules in an emulsion is dependent on the size of the particles of the emulsifier employed.

Pickering adopted this view from his experiments on basic copper sulfate and similar substances. He found that when oil is broken into small globules by being forced through a syringe, and these globules are placed in contact with a number of solid particles, the latter will be attracted to the globules, preventing them from coming into contact and coalescing

with their neighbors. Whether gravitation or other forces account for such a result, he did not determine. Pickering supported the idea that the size of the globules in the emulsion depends upon the size of the particles of the emulsifier by the fact that an emulsion formed with basic ferrous sulfate has a much finer division of droplets than one formed with copper sulfate, because the particles of ferrous sulfate are smaller than those of copper sulfate. With cadmium and basic zinc sulfates, the particles are comparatively large and the emulsion is coarse. However, the chemical behavior of the emulsifier might account for this, and the size of the particles may not be the determining factor. Pickering's standpoint offers a good explanation for emulsification and is in harmony with the facts observed by him.

On the other hand, Pickering finds it quite conceivable that the globules in an emulsion may be uniform in size, and that their actual sizes in different cases may be in some simple ratio, as seems to have been proved in the case of raindrops (see *Nature*, No. 74, p. 230). This is irrelevant, since raindrops form by condensation of ionic nuclei, while emulsion particles formed by the dispersion of a continuous phase possess no such nuclei (Roberts). Still, this does not help matters much, since it is not evident that a difference in the size of the globules would make any difference in the percentage of paraffin in a given volume. For instance, in the case of spherical globules which are closely packed, *i.e.*, touching one another, the percentage of the total volume occupied by the globules is independent of their size. This percentage, moreover, is 74.048, so that, since emulsions with more paraffin are obtainable, it is evident that the globules in them either are not spherical or else are not uniform in size. In a 99-per cent emulsion of fuel oil, the larger globules appeared to have six or seven times the diameter of the smaller ones; in a 94-per cent emulsion of gasoline, the proportion was about 3:1; the largest globules in this case have only half the diameter of those of the first emulsion. A system of this type, with the interglobular spaces filled with smaller globules, accounts for percentages of paraffin higher than 74, but it does not explain the fact of a simple ratio, which Pickering says is often misleading and must be given special consideration when no explanation of its existence is offered.

Bhatnagar²⁴ noticed that the average size of oil globules is greater in emulsions containing free fatty acids and smaller in emulsions containing free alkali than when neutral oil and soap solutions alone are used in emulsions produced under like conditions. It is interesting to note that the addition of a small proportion of free alkali to a soap solution also decreases the size of the particles and results in clarifying turbid solutions, while the addition of free fatty acids increases both the size of the particles and the turbidity of the solution. According to Bhatnagar, the degree of dispersion is another important factor in the stability of an emulsion; therefore when an attempt is made to arrange various emulsifying agents in the order of their ability to emulsify, the particle size of the emulsifying agents must be taken into consideration. Bhatnagar

also is in agreement with Pickering's viewpoint that the particle size of an emulsifying agent has a decided effect on the degree of dispersion. In another instance Bhatnagar²⁵ states: "But the manner in which any of the properties of the emulsion changes with the progress of coalescence is very complicated and no relationship is known between those physical properties and the average size of the aggregate."

Réné^{220, 221, 222} remarks that Perrin was the first to apply gas laws to dilute emulsions made up of equal globules which act like visible molecules. These gas laws predict and explain the distribution of globules in the equilibrium state of a dilute emulsion under action opposed by Brownian movement. René finds it possible to compare an undiluted emulsion like Perrin's with a compressed liquid, the molecules of which can be studied by applying van der Waals' theory. In fact, what Perrin calls the "osmotic compressibility" of an emulsion, *i.e.*, the way in which the osmotic pressure varies as a function of the concentration of globules, can be determined. The distribution of globules in the equilibrium state must be observed in a vertical column of an emulsion, and the number of globules counted. By means of van der Waals' equation, the molecular weight of a compressed liquid with "invisible molecules" can be determined, in the same way that the Avogadro number can be found by observing a compressed liquid with "visible molecules"; this is possible in an emulsion because there the individual mass of the molecule can be measured. René measured the compressibility of an emulsion having equal globules and found Avogadro's number to be 6.0×10^{23} .

The idea of measuring the distribution of sizes of emulsion globules as an important characteristic of emulsion systems was supported by the experimental results of Finkle, Draper and Hildebrand.⁷⁰ They determined the distribution of the number of droplets according to their diameter in emulsions in which sodium, potassium and cesium palmitate were used as emulsifying agents. The atoms of sodium, potassium and cesium increase in diameter in the order given. They also determined the distribution of sizes of the corresponding emulsions and found that the droplets of oil decreased in diameter as the emulsifying agent was changed from sodium to potassium to cesium palmitate. These results were consistent with the "oriented wedge" theory.* But this was later disproved by Harkins. It has been proved that particle size depends on the amount and intensity of agitation.

Experiments^{257, 258} in which diffused light was applied in determining the distribution of sizes of emulsion globules showed that particles in the disperse phase, droplets of which have diameters at least two or three times the wave-length, can be determined directly by the shape of the curves showing the relation between the intensity of light and the concentration. These curves, expressing mass as a function of distribution, agree with those calculated from microscopic measurements. As may be seen by passing from the sodium soap to those of potassium and cesium, different alkali soaps show an increase in the number of small particles.

* To be discussed further.

Harkins and Keith¹⁰⁸ found that their preliminary experiments were in agreement with those of Finkle, Draper and Hildebrand; but upon more careful elimination of all factors and the use of a more suitable optical system, the distribution curve was found to be the same for sodium, potassium and cesium soaps used as emulsifying agents. Later, Harkins and Beeman¹⁰⁴ found that, although most of the droplets have diameters of about 1.5 microns, so that the peak on the number distribution curve is independent both of the positive alkali ion of the soap and of the oil, there are many more large droplets, if a viscous oil like Stanolax is used, than with a fluid oil like octane. By using magnesium or aluminum oleates, *i.e.*, oleates of bi- or trivalent metals, they obtained water-in-oil emulsions. But, in this case too, the number distribution curves were practically the same as those found for oil-in-water emulsions. No change in the number distribution curve was obtained when an oil-in-water emulsion produced by the use of soap of a monovalent metal was inverted by the addition of a salt of a bi- or trivalent metal. The method of mixing was found also to have an effect upon distribution. Emulsions produced by a high-speed drink mixer, when compared with those made by a motor-driven egg-beater, showed that, while the distribution curves had the same form for the smaller sizes, the size of the largest drop was much smaller in the first case than in the second. In general, the number of large drops decreased with the time of stirring, more rapidly at first than later.

The stability of an emulsion is determined by the coincidence of action of various factors. One of these is the character of the distribution curve of sizes and the pronounced presence of small-sized droplets, as indicated by the existence of a peak in the curve corresponding to a maximum number of certain size droplets. Harkins and Beeman¹⁰⁵ suggested that a determination of the variation of the distribution of sizes of the dispersed droplets of the emulsion with time gives a measure of its stability. S. Berkman²⁰ used a new type of Leitz micro-projection apparatus for determining the distribution of sizes of globules in octane/water and Stanolax/water emulsions, with sodium oleate as the emulsifier. Each number distribution curve was obtained (a statistical method was used and the law of great numbers considered) by calculating and measuring an average of 1500 to 2000 droplets. The results obtained for the octane/sodium oleate/water systems indicate that all distribution curves of sizes have a maximum corresponding to droplets of one micron in diameter. This maximum is independent of the concentration of the emulsifier, but the absolute percentage of droplets of one micron in diameter varies until the emulsion reaches equilibrium, the absolute percentage of these droplets becoming smaller when the percentage of droplets of the next size becomes higher. When an emulsion appears to be durably stable (15 days, 2 months) (that is, reaching a static, not a dynamic, equilibrium) a deviation is obtained in the other direction, *i.e.*, it contains 5 to 6 per cent of oil droplets 0.5 micron in diameter and a higher percentage of oil droplets 1.5 and 2 microns in diameter. Before a "durable" equilibrium

corresponding to the stable state of the emulsion is reached, deviations in both directions, from the maximum to one micron in diameter, are observed. The courses of reaching equilibrium for octane/water emulsions with various concentrations of the emulsifier differ, as shown by the change in the absolute percentage of the various sized droplets in the number distribution curves. The absolute percentage of droplets of the same size in different concentrations of soap does not change much in the case of octane emulsions.

The number distribution curves of sizes for Stanolax emulsions are about the same as for octane emulsions, and even the absolute percentage of droplets of various sizes is not much different. The maximum of the curve is at the one micron size. The character of the distribution curves is also the same on addition of oleic acid or sodium hydroxide. The stability of an emulsion seems to depend not only upon the distribution of sizes of particles of the disperse phase, when the system reaches equilibrium, but also upon the rate of increase in the amount of medium-sized particles, which can be produced by the addition or the presence of electrolytes. The durable stability of an emulsion of octane and water with $0.1M$ sodium oleate + $0.01M$ sodium hydroxide is less than that of an emulsion of octane and water with $0.1M$ sodium oleate. The rate of increase in the number of medium-sized particles is pronounced in the case of heavy paraffin/Stanolax oil emulsions with a low concentration (0.01 or $0.005M$) of sodium oleate, which corresponds to a rather unstable system, or to a system without durable stability.

In order to study more thoroughly the kinetic changes as reflected in the distribution of sizes, it is necessary to take into consideration small rates of change; therefore a mathematical analysis of the results obtained was required. The distribution of sizes and the corresponding percentage of droplets obtained experimentally for each emulsion were plotted directly as integral curves in a coordinate system, and from these integral curves, derivative curves were constructed. The shape of the differential curves and the level of the percentage of maximum small-sized globules on the derivative curves reflected the presence or absence of hydrolysis, high or low concentration of the emulsifier, and the relative age of the emulsion. The fact that stability of emulsions is generally determined by allowing the emulsion to stand until the disperse phase collects *en masse* to an extent decided upon by the individual observer greatly favors the new method proposed by S. Berkman²⁰ for measuring the most important characteristic of an emulsion, namely, its stability.

Recently, Bailey, Nichols and Kracmer^{6,7} described a method for calculating, by means of an integraph, the relation between the optical absorption coefficient of a colorless emulsion and the radii of particles from a series of "weight-optical" distribution curves obtained for Nujol/aqueous glycerol emulsions. The particle size distribution is expressed as a relationship between dc/dr and r , where dc/dr is proportional to the weight of particles having radii between r and $r + dr$. The low-speed Svedberg ultracentrifuge gives the relation between $d/(KC)/dr$ and r , where K

is the apparent absorption coefficient of a suspension of particles with a radius r . If the weight-optical distribution is represented by the equation $d(KC)/dr = f_n(r)$ and the variation of the absorption coefficient K with r by the equation $1/K = F(r)$, then it follows that

$$\int_{r_{\min}}^{r_{\max}} f_n(r) \cdot F(r) = 1$$

Thus, each weight-optical distribution is expressed by a particular $f(r)$ and $F(r)$ which must be calculated from a series of simultaneous integral equations equal in number to the experimentally determined weight-optical distribution.

Inversion of Phases in an Emulsion System and Factors Influencing It

It is an established fact that in most cases three components are essential for the formation of a stable emulsion, namely, two liquids and an emulsifying agent. Theoretically, two types of emulsions are possible, according to which a liquid is dispersed as droplets. The inversion point of emulsions is defined as that point at which a change from an oil-in-water to a water-in-oil emulsion, or vice versa, takes place. In all probability, this point also marks a region of instability and hence is of practical importance from the standpoint of breaking emulsions. The work on emulsions indicates a tendency to study the factors affecting the inversion point. Seifriz,²³⁵ investigating the relation between emulsion inversion and surface tension of oils which are themselves factors determining the emulsion type, obtained data for eight oils which revealed no apparent relation between their surface tension values and the inversion point.

Wilson²⁸⁶ states that to reverse an emulsion type a substance that will produce the opposite emulsifying effect must be added. When sodium oleate is used as an emulsifier, the salt is hydrolyzed and is therefore present as sodium hydroxide, oleic acid and sodium oleate, rather than as a simple sodium salt. By using an excess of oleic acid with sodium oleate, an emulsion of the water-in-oil type results upon homogenization, when the oil is in excess of 62 per cent. The type of emulsion obtained was found to be affected more by variations in the sodium hydroxide than in the oleic acid.

The inversion of a stable oil-in-water emulsion made up of a mixture of 1.4 g of oleic acid plus 70 cc of benzene in 28 cc of water containing 2 cc of 0.1*N* sodium hydroxide was observed when the amount of sodium hydroxide was increased to 4 cc (corresponding to 26 cc of water). The emulsion thus formed was a water-in-oil emulsion, the 6 to 14 cc water-in-oil emulsion corresponding to the 16-20 cc oil-in-water emulsion. The inversion in phases was explained by decrease in the interfacial tension caused by increase in the concentration of the soap, as well as by an excess of oleic acid in benzene.

Hemmer,¹¹⁷ investigating the inversion of emulsions of xylene, carbon tetrachloride and soap solution, found the inversion point, which was above the critical geometrical point (74.05 per cent disperse phase), to be dependent on the physicochemical properties of both phases. He stated that the inversion point rises with a decrease in surface tension and that it corresponds also to a definite value of $\text{pH} < 11-12$, above which the inversion point drops. This is observed with both the oil-in-water and water-in-oil types of emulsion. Therefore, both types may be obtained below the critical geometrical point under suitable conditions.

It has been assumed by Robertson²²⁸ that at the critical ratio of water to oil, as much soap is present as can surround the surface of the oil droplets without formation of intermediate spaces of more than molecular dimensions. The amount of soap collected at the contact surface of oil and water is determined by the distribution coefficient of soap between the two phases, according to Gibbs' equation: $\Gamma = \frac{-C}{RT} \cdot \frac{d\sigma}{dc}$. When this relation of both substances becomes smaller than the critical one, the system can no longer exist; instead, a system is formed having a greater surface, i.e., water, or a dilute emulsion of oil-in-water, emulsified in oil. Robertson states that the mechanical force which comes into play in the formation of the emulsion assures the largest possible contact surface between oil and water. If this surface possesses considerable surface tension, as is the case when insufficient soap is present to surround the droplets completely, the system is destroyed and a new one formed, giving the next largest contact surface, in which water droplets or droplets of a dilute emulsion of oil in water are dispersed.

Parsons and Wilson¹⁹⁰ investigated the inversion of phases: (1) in the case of highly purified Nujol; (2) in Nujol/water systems with added commercial oils; and (3) in emulsions of various commercial oils. In general, these investigators found that emulsifying agents which tend to produce an oil-in-water type of emulsion are those which are either soluble in water, i.e., the external phase, or those more readily wetted by water than by oil. Correspondingly, for the water-in-oil type, solubility or greater wetting ability of the emulsifying agent in the oil phase is a necessary prerequisite. Parsons and Wilson state that no critical ratio was found when magnesium and sodium oleates were used as agents for Nujol emulsions. Inversion of phases implies that the emulsifier can stabilize either form of emulsion, forming a protective film around the small particles. This opposes the theory of Bancroft¹¹ who advanced the first theory of the relation between the type of emulsion and the stabilization agent. Further, he believed that the interfacial film between the disperse phase and the dispersion medium is a film having two surface tensions, one on the water side and the other on the oil side.

It has been proved experimentally⁴⁷ that for the oil-in-water type of emulsion, formed by monovalent cations dispersed in water, the surface tension is lower on the water side than on the oil side, the coherent film

formed by the soap tending to curve in such a manner as to enclose the oil globules in water, and that the water-in-oil type, in which the film is composed of soaps of di- or trivalent cations dispersed in the oil, has a lower surface tension on the oil side and the film has a tendency to curve so as to enclose the globules of water in the continuous oil phase. Clowes presented this schematically in Fig. 3.

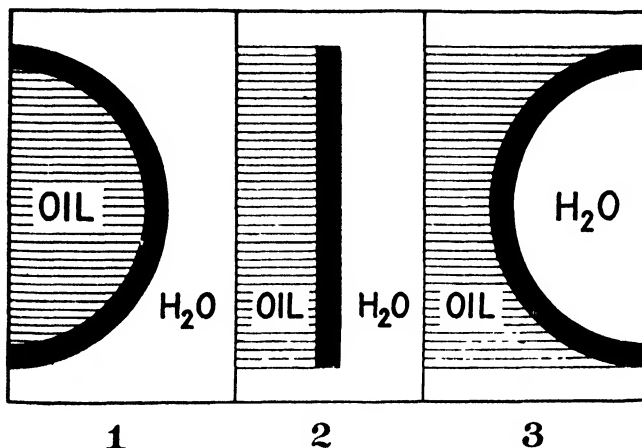


FIG. 3. (Clowes⁴⁷)

	1	2	3
Emulsifying agent or film	Sodium oleate alone or sod. oleate in excess of calcium oleate equiv.	Equiv. chem. proportion sod. oleate and calcium oleate.	Calcium oleate alone or calcium oleate in excess of sodium oleate equiv.
Emulsion formed	Oil-in-water.	Critical point.	Water-in-oil.

According to this theory, the nature of the stabilized film would change in order to produce inversion, and the only effect of increasing the ratio of the disperse phase would be to allow the excess disperse phase to form a separate, non-emulsified phase. In general, no true inversion point was noticed when the volume ratio alone was varied but, as would be expected, there is a maximum amount of oil which can be emulsified; above this point, the emulsion breaks.

Clowes⁴⁷ supported Parsons' idea that the film around emulsion particles has the properties of a plastic solid, and that if the emulsifying agent could be altered so that it would be wetted more by the internal phase, the emulsion would be inverted. Clowes was able to change an oil-in-water emulsion stabilized by sodium oleate to a water-in-oil emulsion by adding a calcium salt which formed an oil-soluble soap which was insoluble in water. This inversion was confirmed by microscopic examination, which showed that the oil globules (b) become distorted and elongated near the critical point at which large masses of water (A) and oil (B) are actively streaming. Beyond the critical point the emulsion

shows large drops of water surrounded by oil. In the water globules there are still smaller globules of oil exhibiting rapid Brownian movement. When this particular Brownian movement ceases, complete reversion to the water-in-oil type takes place. Fig. 4 presents the scheme of inversion with reference to the appearance of the emulsion given by Clowes.

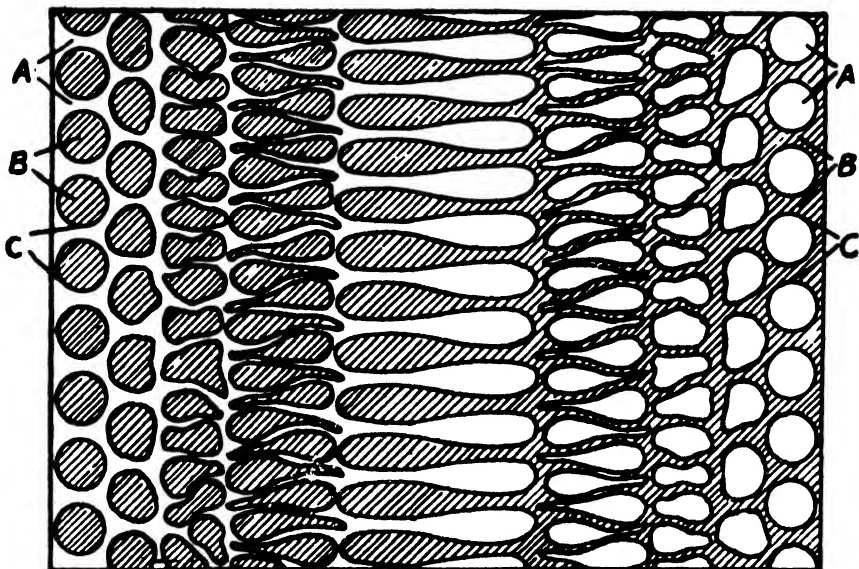


FIG. 4. Inversion of Emulsions (Clowes).

A = water B = oil C = adsorbed film

Clowes⁴⁷ found that emulsions of oil in water are formed whenever there are more than four molecules of sodium hydroxide to one of calcium chloride; emulsions of water in oil, whenever there are less than four molecules of sodium hydroxide to one of calcium chloride; at those points at which the ratio of sodium hydroxide to calcium chloride is exactly 4:1, neither type appears to predominate.

These results were obtained from a study of emulsions of olive oil which, on account of its composition and the impurities present in it, undoubtedly behaves differently from mineral oils. Clowes observed, moreover, that if sodium oleate and calcium oleate are present in approximately equivalent amounts in a mixture of water and benzene, no emulsion can be formed. Results obtained by Wellman and Tartar²⁸⁰ contradict those reported by Clowes; therefore, Clowes' interpretation is not applicable to all soap emulsion systems.

Briggs³¹ explained that sodium oleate and calcium oleate are mutually antagonistic emulsifying agents, and that when they are present in the right proportions, each neutralizes the emulsifying action of the other

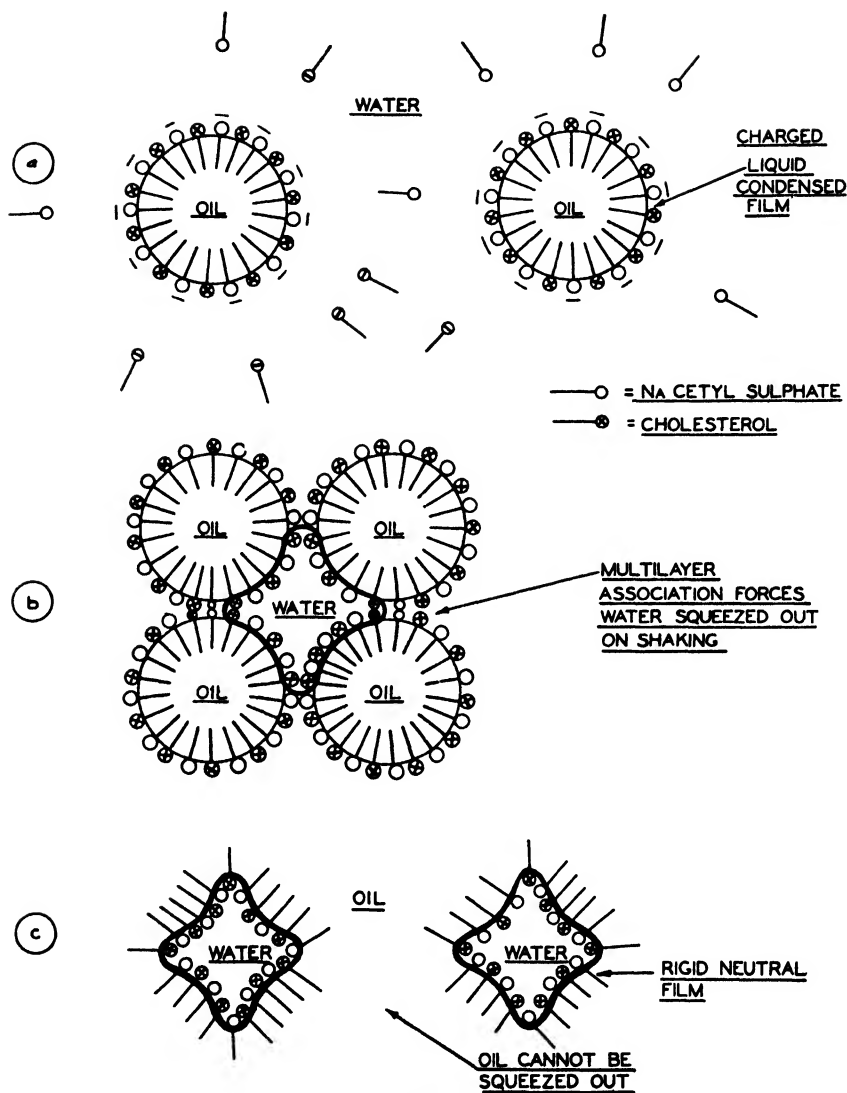


FIG. 5.

Sodium oleate produces emulsions of oil in water, whereas calcium oleate produces emulsions of water in oil (benzene). Bhatnagar²⁴ found that the 4:1 ratio mentioned above was affected by the volume ratio of the two phases, as well as by other ions, and that it changed with different soaps. As Clowes first discovered, reversal of phase in oil emulsions can be caused by electrolytes, Bhatnagar adding that each of the emulsions investigated can be inverted by "suitable" electrolytes. Therefore, he states, a water-in-oil emulsion can be transformed by anions, such as

OH' and PO_4''' , whereas the reverse transition is brought about by the cations H' , Al''' , Fe'' , and Th''' .

Two conditions have been given by Schulman and Cockbain^{234a} as essential for the formation of Nujol-in-water emulsions: (1) the interfacial film must be electrically charged, and (2) it must be in a condensed liquid state. Furthermore, these investigators^{234b} deduced that, in order to produce phase inversion of such emulsions, the electric charge on the oil droplets must be removed and the interfacial film must acquire considerable rigidity. The addition of polyvalent ions (or charged molecules containing many polar groups capable of multiple-point interaction with the film-forming substances) to Nujol-in-water emulsions stabilized by a complex of the opposite charge produces the desired effect. The interfacial film is discharged, water is squeezed out from the interfaces of the oil droplets, forming water "sacks" dispersed in oil, and the film molecules which are interlaced by the polyvalent ions cause a marked increase in the rigidity of the interfacial film.

A Nujol-in-water emulsion stabilized by a liquid condensed mixed film, such as cholesterol plus sodium cetyl sulfate treated with polyvalent cations (Ca^{++} or Ba^{++}) is directly inverted into the water-in-oil type as shown in Schulman and Cockbain's diagrammatic sketch, Fig. 5. The cations remove the diffuse double-layer of sodium cetyl sulfate, and the adsorption of cations destroys the negative charge on the oil droplets (Fig. 5a). Since the molecules of the interfacial film align themselves with their polar heads, water molecules are squeezed out from between the oil droplets (Fig. 6). In Fig. 5b, the oil droplets are in a state of coalescence after removal of the charge, a crystal packing arrangement is effected, and water "sacks" float away.

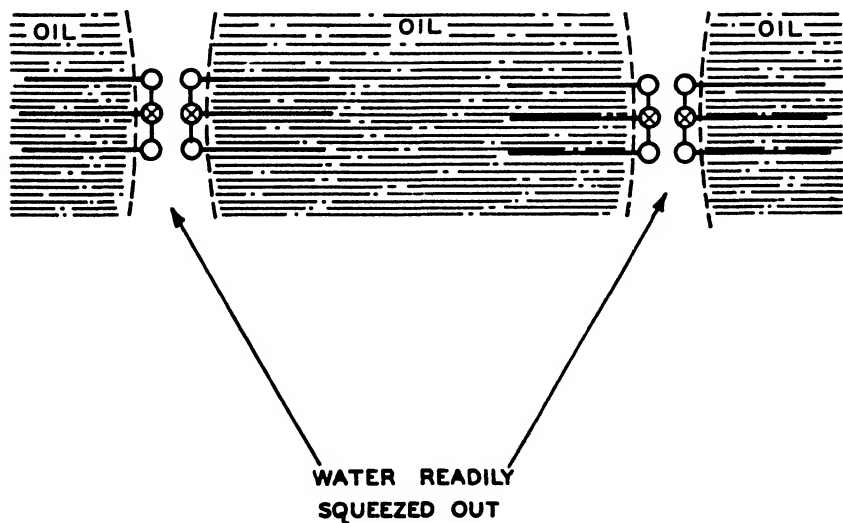


FIG. 6.

In Fig. 5c the emulsion is of the water-in-oil type. The hydrophobic chains of the molecules of the film adhere to the oil molecules of the continuous phase as ionic head groups in interfacial films adhere to water molecules in emulsions of the oil-in-water type.

Water "sacks" of irregular shape due to the rigidity of the interfacial film are typical of water-in-oil emulsions. No coalescence of the water "sacks" takes place, because the oil cannot be squeezed out from between them. The molecules of the interfacial film in the water-in-oil emulsion have their long hydrocarbon chains directed outward from the water "sacks."

Inversion of phases in an emulsion system may be the result of a sudden addition¹⁷⁶ of a large amount of water, rapid stirring, or the addition of an emulsifying agent. Parke and Graham¹⁸⁹ investigated the effect of adding water to both types of emulsions with reference to their viscosity. The emulsions investigated were (a) benzene (or Tetralin) and oleic acid in sodium hydroxide solution, and (b) benzene (or Tetralin) and sulfonated fish oil in sodium hydroxide solution. When water was added in increasing amounts, the viscosity decreased rapidly with increase in added water to emulsions of the oil-in-water type (a). For emulsions (b) the viscosity increased with the addition of water, passing through a steep maximum when about 25 per cent of water was added, and decreased on further addition of water. Emulsions having 20 to 25 per cent water content are of the multiple type, while those having 27.5 to 55.0 per cent water content are of the dual type, and there is a break in the viscosity when about 60 per cent of water is added.

Bhatnagar²⁴ also investigated the effect of dilution on the reversal of phase by electrolytes. He found that the greater the dilution, or the greater the distance between the oil particles in an emulsion, the larger the amount of multivalent electrolyte is required to bring about reversal of phases. He observed that free fatty acid and free alkali shift the inversion point in opposite directions. Tervalent electrolytes have a greater effect on the inversion of an emulsion than bivalent ones. The difference in the percentage of electrolyte required to bring about reversal of phases with different soaps indicates the probability of a difference in their protective action. Bhatnagar's results show that the soaps, such as sodium and potassium stearate, sodium and potassium palmitate, and sodium and potassium oleate, can be arranged in the order of their protective action with respect to paraffin oil.

Briggs³¹ proved a similar antagonistic action for solids, showing that, among solid emulsifiers, carbon black emulsifies water in oil, and that finely divided silica emulsifies oil in water. It is evident, then, that the nature of the emulsifier definitely controls the type of emulsion system formed. Parsons and Wilson¹⁹⁰ considered the mechanism of inversion to be first, a chemical reaction destroying the film, then a breaking of the emulsion, with formation of a polyvalent soap in the oil, and finally emulsification with the phases inverted. In general, according to these investigators, sodium oleate, a monovalent soap, produced more stable

emulsions than polyvalent soaps in the case of a Nujol system. When the equivalent concentration of a polyvalent ion exceeded that of a monovalent soap, complete inversion resulted; when it was less, there was partial inversion. Hatschek draws attention to the fact that if the emulsifier in an oil emulsion is a colloid other than soap, gum arabic for example, the emulsion will not be inverted when a bivalent electrolyte is added to it.

Bhatnagar²⁴ carried out experiments, keeping all other conditions constant, to determine the action of electrolytes on the inversion point by changing the volume ratio of the two phases. The results obtained indicated that the proportion of multivalent electrolyte, barium nitrate or aluminum sulfate, required to bring about inversion of the phases in a paraffin/water/lithium stearate system (0.12 millimol) is directly proportional to the volume of the aqueous phase and inversely proportional to the volume of the oil phase. Similar results were obtained with other soaps and electrolytes.

Tartar, Duncan, Shea and Ferrier,²⁶⁵ in their study of the effect of electrolytes upon emulsions, found that the nature of the oil also influences the type of emulsion formed. Emulsions of benzene, toluene, and xylene, with water and sodium oleate as an emulsifier, formed the water-in-oil type when monovalent cations equal to those of the soap were added. The inversion zone for benzene was found to be between 0.25*N* and 0.45*N* sodium chloride; for toluene, 0.25*N* and 0.40*N* sodium chloride, and for xylene, 0.30*N* and 0.45*N* sodium chloride. The inversion point in the case of a benzene emulsion was shifted somewhat when sodium hydroxide solution was used together with sodium chloride solution, whereas in toluene and xylene emulsions the breaking point was not markedly influenced by the addition of sodium hydroxide. The emulsion consisting of 12 cc of benzene and 2 cc of aqueous solution of sodium oleate as emulsifier was destroyed by addition of various acids, such as hydrochloric, oxalic, etc., *i.e.*, when approximately enough acid was added to decompose the emulsifier.

Abramowitsch-Dvoretzkaja¹ states that soaps of low molecular weight acids produce inversion of petroleum type emulsions at higher concentration of the added electrolyte than do soaps of higher molecular weight acids. Under the influence of sodium hydroxide and sodium sulfate, sodium soaps of naphthenic acids give both types of emulsion, oil-in-water as well as water-in-oil. Gas oil and cylinder oil distillates also yielded both types of emulsion. It is stated that lowering of temperature promoted formation of the water-in-oil type.

Newman's investigation¹⁸⁰ questioned the formation of a water-in-oil type of an emulsion by a mere increase in the oil phase. Experiments by Robertson²²⁶ gave evidence favoring the formation of both types of emulsion by a change in the volume ratio of the separate phases. Bhatnagar²³ has shown that in very low concentrations of the emulsifying agents the phase ratio alone determines the formation of either type of emulsion in the case of viscous oils like B.P. paraffin and olive oil, but

this is not true in the case of light oils like kerosene. It was also pointed out by Bhatnagar that the stability of a water-in-oil emulsion obtained by simply increasing the proportion of oil is less than that obtained when the nature of the emulsifier aids the stability. Sanyal and Yoshi²³⁰ found that the nature of the emulsifying agent is more significant than the volume ratio when the concentration of a soap solution is increased to about one per cent, and that oil-in-water emulsions are stable only with a soap like sodium oleate. Water-in-oil emulsions were formed when the concentration of the emulsifying agent was less than one per cent and the oil used was viscous. In these cases, the volume of both phases is an important factor in determining the type of emulsion formed. These investigators state also that the mechanics of dispersion can be maintained uniform with the use of various emulsifying agents. However, Roberts²²⁵ states that the presence of emulsifiers does not appreciably alter the dispersion characteristics of the system. Oleic acid reverses the phase relations with alcohols, dimethyl aniline, nitrobenzene and Stanolax, and causes carbon tetrachloride, benzene and heptane to disperse in water. Magnesium palmitate causes the water to become the disperse phase. Sanyal and Joshi deduced therefrom that the character of the film formed by the magnesium palmitate at the liquid/liquid interface was such as to protect water droplets in oil, but not oil droplets in water. The instability of oil droplets in water in the presence of magnesium palmitate is no more related to shapes and sizes of molecules than is any other dispersed system in the presence of an emulsifying agent.

The term "dual emulsions" is applied to emulsions of the same pair of liquids having the same emulsifier, but present in opposite types, such as oil-in-water and water-in-oil emulsions. These emulsions, when studied by Cheesman and King,^{44b,44c} were prepared with the pairs water-amy alcohol and water-kerosene, using as emulsifying agents for both systems sodium oleate, magnesium oleate, sodium cetyl sulfonate, finely divided carbon (pigment black) and bentonite. The emulsions were prepared by three methods. The stability was measured by determining the time required for 5 cc of the disperse phase to separate from 50 cc of the emulsion. In nearly every case the phase-volume ratio and the proportion of the emulsifying agent were identical for both the oil-in-water and water-in-oil types. The results obtained make questionable the rule that a given emulsifying agent is capable of stabilizing an emulsion of one type only.

In studying emulsions prepared from amy alcohol and an electrolyte solution, Cheesman and King^{44b,44c} ascertained the applicability, over a wide range of pH, of Lederer's formula: $dV/dt = K(1 - V).V^{0.5}$, where V is the disintegrated amount; t , time; and K , constant, characteristic of the stability of emulsions. In the case of alkali emulsions, the dispersion conforms to this relationship, while it is not fulfilled with more stable and acid emulsions. The influence of the hydrogen and hydroxyl ion concentration upon the dispersion process is clearly revealed.

Nagelstein^{170a} ascertained that the stability of the Cheesman and

King emulsions is affected not only by the alkali dissolved from the glass containers, but also to a greater extent by the atmosphere and distribution of the enclosed air. The stability of emulsions is affected by the enclosed air in two ways: (1) by purely mechanical means, and (2) by temperature variations which bring about changes in concentration by alternate vaporization and condensation.

Woodman²⁹⁰ advanced a theory according to which the formation of dual emulsions is due to differences in the distribution of the emulsifier between the two liquid phases. He found, for emulsion systems containing cresylic acid, phenylhexaline or methylhexaline, water and gelatin, that by the formation of the oil-in-water type with cresylic acid, for example, the aqueous phase contains more gelatin than by the formation of a water-in-oil emulsion. In another work, Woodman²⁹³ emphasized the possibility that gelatin may give emulsions with cresols of the oil-in-water and water-in-oil type, depending upon the phase-volume relationship whereby the excess of one liquid phase is the determining factor. The excess in water gives the oil-in-water type and vice versa, and by a definite phase-volume relation, dual types of emulsions may be obtained. In certain instances^{113,292} both types of emulsion formed when the constituents were not varied in amount, the mechanical agitation in their preparation being the decisive factor.

Rehbinder,²¹⁸ studying toluene/sodium oleate/water emulsion systems, used magnesium sulfate as an "invertor," assuming that during the change of phase an intermediate stage takes place, characterized by a foaming interface emulsion, which permits following quantitatively the phase change in emulsions.

Bancroft,^{10,11} as well as Newman,¹⁸⁰ believed that whether one liquid is emulsified in a second, or the second in the first, depends on the nature of the emulsifier. A hydrophilic colloid tends to make water the external phase and a hydrophobic colloid tends to make it the internal phase. The emulsifying agent in petroleum is dominantly an oil-soluble colloid, because petroleum emulsions are mostly of the water-in-oil type. Magnesium oleate was found to be the best emulsifying agent tried up to 1914 for making an emulsion of water in benzene. These emulsions become much more stable if a little sodium oleate is also present. But whether emulsions of water in benzene or of benzene in water are obtained depends upon the relative proportions of magnesium oleate and sodium oleate. Stamm and Kraemer²⁵⁶ report that in mixtures of water with isoamyl alcohol, *n*- and isobutyl alcohol, α -ethylacetate, dimethyl aniline, nitrobenzene, chloroform, carbon tetrachloride, benzene, or heptane, the dispersed phase is the less viscous. Perhaps the changes in viscosity observed by Caldwell in such mixtures are active here. The addition of oleic acid enables water to become the disperse phase. The addition of magnesium palmitate has the opposite effect. If glycerin is used without an emulsifying agent, it is always the disperse phase. The addition of potassium palmitate makes it the continuous phase.

Seifriz's experimental data²³⁷ indicate the possible influence of acidity

on phase reversal. That the pH value is a factor in phase reversal is true in certain cases, but not in others. Hydrogen ion concentration must affect the reversal of an emulsion by acting on the emulsifier, possibly on its hydration power. Consequently, the effect of pH will differ in emulsions with different emulsifiers. When dilute solutions of alkali are used, a comparatively large amount of free fatty acid is left unneutralized in the system. The presence of free fatty acid or free alkali makes the system more complex and, in addition, seems to have a definite effect on the equilibrium of the emulsion. Comparable results can be obtained only by using a neutral oil and soap solution.

The question why different types of emulsions, such as oil-in-water or water-in-oil, are formed, Briggs³⁰ answers by saying that it is generally agreed, without a satisfactory explanation, that the liquid which wets the emulsifier more thoroughly under the conditions of the experiment tends to become the continuous phase; the less wetted liquid is broken up into droplets and becomes the disperse phase.

Weichherz,^{276,278} in his article, "The Knowledge of Emulsions," says that the assumption that hydrocarbons form only oil-in-water * emulsions with alkali soaps is false. He further reports that small percentages of phenols, alcohols and water promote the solubility of alkali soaps in hydrocarbons. The systems investigated up to the present contained small proportions of soap, and the significance of the solubility of the alkali soaps in the hydrocarbons was neglected. On the one hand, it was proved that the solubility of the alkali soap in the hydrocarbon was unquestionable; on the other hand, it was observed that at high soap concentrations (according to the unfavorable soap distribution coefficient) water-in-oil emulsions were formed.

Phase reversal can be caused by a change in soap content in terms of phase-volume relation, the soap being distributed between the two phases, and some kind of distribution equilibrium is obtained. At the boundary surface, soap is adsorbed from both phases, and this adsorption equilibrium prevails over the distribution equilibrium. The boundary phase consists of soap/water micelles which are adsorbed by the aqueous phase when the soap content is small. With a large soap content or a relatively small aqueous phase, the soap concentration in the oil phase is considerable, and at the boundary surface hydrocarbons and soap micelles become adsorbed. The phase reversal of emulsions follows a certain phase-volume relationship with critical soap content when a critical phase-volume is selected. The critical point is not sharp, and limits can be given only within which neither of the emulsion types is stable. Phase reversal was obtained by the addition of multivalent salts. An ionic antagonism is assumed between the multivalent and monovalent salts, the antagonism existing in the relative adsorption of ions from the salts at the boundary surface. Simultaneously, this selective ion adsorption

* A great deal of conflicting evidence on types of emulsions formed with alkali soaps appears to be due to the use of old dilute soap solutions which have hydrolyzed, producing oil-soluble acid-soaps that promote water-in-oil emulsions.

causes a change in the wettability of the soap. As for ion antagonism in Clowes' sense, Weichherz says there can be no question that on addition of calcium chloride the water-soluble soap becomes insoluble in water, but soluble in hydrocarbons, being converted into a stoichiometrically defined calcium soap. If sodium chloride is added to this system, the calcium soap is converted into sodium soap which becomes soluble in water, and an oil-in-water emulsion is again formed. The ion antagonism exists only as long as the percentage of sodium chloride added does not reach the precipitation limit for the soap, at which it becomes insoluble in water in spite of mass action. Therefore, the distribution of soap in the hydrocarbon phase is improved and the formation of water-in-oil emulsions is more plausible. At the limit, the ion antagonism between calcium chloride and sodium chloride is ended and a definite phase reversal is produced. The apparent ion antagonism exists at only very low soap concentrations.

Summarizing our knowledge of the conditions influencing the reversal of phases in an emulsion system, we may say that no sharp line of demarcation can be drawn between the conditions suitable for the formation of one type or the other. Only by working under identical conditions and using the same emulsion system with the same emulsifier, or at least an emulsifier of a class with the same properties, can we expect to find the conditions of volume, composition, presence of electrolytes and their valence favorable for the transition of one system to another.

Adsorption of the Emulsifying Agent at the Interface, Film Formation, and Variations in the Nature and Thickness of a Film as Factors in the Stability of an Emulsion

In the section on surface tension, mention is made of the relation existing between the surface tension, the adsorption of the emulsifier, and the stability of the emulsion system. The relationship between surface tension and concentration on a thermodynamic basis was first pointed out by Gibbs. This he formulated into the well-known Gibbs equation:

$$\Gamma = \frac{-C}{RT} \cdot \frac{d\sigma}{dc}$$

where Γ is the increase in concentration at the boundary surface; C , the concentration of the solution; σ , its surface tension; T , the absolute temperature; and R , the gas constant. The Gibbs equation shows that three factors, *i.e.*, solubility, surface tension and adsorption, are closely related. The validity of the Gibbs equation was tested by Donnan and Barker⁵⁸ for nonylic acid; they found, by direct measurement, that the adsorption was 1.0×10^{-9} gr/sq. cm, whereas the equation gave 6.0×10^{-7} gr/sq. cm. Likewise, other quantitative investigations of the Gibbs equation have not given concordant results. The adsorption at the interface, as found by experiment, has usually been far greater than that called for by the reduction of the surface tension. This is brought out in Table 9.^{153, 154}

Table 9. Comparison of Interfacial Adsorption as Found and Calculated from Gibbs' Equation

Substance	Adsorption (gr/sq. cm of substance, assumed to be in the form of an undissociated salt or in chemically equivalent ionic proportions)	
	Found	Calculated
Sodium glycocholate	5.0×10^{-8}	7.0×10^{-8}
Congo red	3.7×10^{-8}	1.1×10^{-7}
Methyl orange	5.5×10^{-8}	1.2×10^{-7}
Sodium oleate	10^{-8}	10^{-8}
Caustic soda	1.5×10^{-7}	7.5×10^{-7}

In fact, the experimental evidence as given in this table shows a far greater surface adsorption in the case of colloids than with substances to which Gibbs' equation strictly applies.

Adsorption, according to the Gibbs-Thomson principle, is such that the dispersed substance accumulates at the boundary surface. If a colloid is present, characteristic irreversible changes may take place, such as the formation of skins or films. The formation of skins, for instance, often interferes with the accurate measurement of surface tension and may cause a difference between calculated and experimental values.²⁸⁷ Shorter^{246,247} states that Gibbs' thermodynamic theory of the changes in the surface layers of solutions involves the assumption that they are reversible. Many of the most interesting and important changes in chemical composition at surfaces, however, involve actions which may be either irreversible or reversible, but are extremely slow. Shorter pointed out that these include surface changes of many colloidal or semi-colloidal solutions. An extreme case of irreversibility is offered by aqueous solutions of albumin. If a hydrocarbon oil is shaken with a solution of albumin, an emulsion is formed which lasts a long time even if the solution around the droplets is replaced by pure water. In this case, the quasi-solid skin around each droplet differs from the albumin in the solution, and the change produced in the surface layer is a kind of coagulation. The question of the reversibility of the process of concentration of a dissolved substance in the interface layer (adsorption) must be considered important in connection with the stability of emulsions on dilution. Emulsions made with soap as the emulsifying agent are unstable when diluted beyond a certain point. The addition of certain other colloids increases their stability in this respect. It is a fact that protection against the breaking of an emulsion is usually assumed to be due to a film of some kind at the interface. The nature and properties of this film are only vaguely understood. The tendency to coat liquid droplets with an adsorbed layer, giving stability to the droplets of the disperse phase, is observed with some emulsifying agents. If fairly large droplets of a solution of saponin, a good emulsifying agent, are allowed to fall into a second liquid, they do not immediately assume spherical form, as would be expected, under the influence of surface tension. The droplets often retain their elongated form for a considerable time, indicating that the coating of the emulsifying agent possesses considerable rigidity

Bancroft¹¹ writes that the emulsifying power of saponin is easily understood when one observes the form of the drops produced as they flow through cottonseed oil. A drop of saponin solution as it is detached takes the form of a pear with the stem plainly visible. This stem, the remainder of the filament drawn out as the drop is detached, may remain visible for many minutes. Wilson and Ries²⁸⁷ carried out similar experiments and made photographs of drops of oil containing saponin that had been allowed to fall into a salt solution. The drops formed under these conditions also have peculiar properties, in that they maintain irregular shapes and even sharp points for long periods of time. These investigators pointed out that by comparing the photographs taken 30 minutes or more after the formation of the droplets, it appears that there is less tendency to form plastic solid films at interfaces than at free surfaces, although they are undoubtedly formed in some of the more concentrated solutions of saponin and sodium stearate. Lower concentrations give films apparently of high viscosity; but if they have a definite breaking point characteristic of plastic solid films, it must be small compared with the forces of surface tension at concentrations below 1 and up to 5000. One factor which might account for the apparent greater difficulty in obtaining evidence of the presence of plastic solid films between liquids is that all the surfaces studied in this case were curved, whereas the surface films previously investigated were plane.

Solutions which form plastic solid films give high surface tensions because the yield of the plastic solid film is added to the true surface tension. Wilson and Ries think that solid plastic films are of colloidal rather than of molecular dimensions. Undoubtedly, similar resistant films form at the surfaces of the much finer droplets in emulsions. It is claimed that under the microscope some emulsions plainly show the films separating the globules. In the case of several emulsions, notably one of olive oil and saponin solution, Ramsden^{211, 213, 215} was able to prove the existence of membranes separated out from the liquid/liquid interface. The adsorbed layer of emulsifying agent manifested itself in the extreme viscosity at the interface, the deformed appearance of the dispersed globules, and the actual appearance of semi-opaque membranes. Ramsden states that some adsorption surfaces are extremely viscous or even rigid—for example, saponin and nearly all the proteins—and the adsorbed particles must then be directly in contact. Others are freely mobile—for example, quinic acid soaps—and the particles must then be either more widely spaced or so oriented that only “liquid” cohesions come into action. In many cases, where adequately durable bubble films are obtainable, the interference colors develop as the film becomes thinner, form in horizontal bands when the surfaces are mobile, but are chaotic when the surfaces are rigid. In the case of saponin, Ramsden found evidence that, before adsorption has become too great, every molecule of saponin coming into the surface region is propelled to the actual interface and, although still soluble, is kept there permanently. Up to this stage adsorption is absolute and independent of the concentration of the bulk solution.

No existing adsorption equation is accurate, according to Ramsden, since it cannot take into full account the effects of varied orientations, intramolecular strains and molecular spacings at different levels of the surface region. Mixtures of a solute, which form rigid surfaces with a solute of much greater tension-lowering power, such as sodium oleate which does not form a rigid surface, have free surfaces. Hence the solute which lowers the tension to a "greater" extent, although less adsorbable in quantity, appears to be preferentially adsorbed. Ramsden is uncertain whether the solute which might form rigid surfaces is completely excluded from the surface regions, since some of it might conceivably be present in capsules in the other solute. If the adsorbed material is soluble, the surface becomes mobile; but if it is insoluble, the surface retains some of its original rigidity. However, the possibility is not excluded that both substances may be present in the interface, possibly in equal proportions or even with an excess of the solid-forming material. In such cases, it is only necessary to assume that one material acts as a "solvent" for the other, so that mixtures of the two may easily give rise to mobile films. Physically, such an effect is readily explainable on the basis that the "solvent" component decreases the intermolecular cohesion of the "solid" component, so that the mixture is liquid over a wide range of concentrations. Interfaces between appropriate aqueous solutions and liquids immiscible with water, as well as emulsion interfaces, are mobile in some cases and rigid in others, regardless of whether the emulsions are of the oil-in-water or the water-in-oil types. Clowes⁴⁷ demonstrated similar enveloping films in emulsions of olive oil. Clark and Mann⁴⁵ found these films in emulsions of benzene and kerosene stabilized with egg albumen.

According to Bancroft,¹¹ as well as to Holmes and Cameron,¹²⁷ the stability of any emulsion is largely due to the nature of the interfacial film which is formed. The interfacial film may be regarded as an equilibrium product resulting from precipitating action on the water side and peptizing action on the oil side. When equilibrium is reached the amount of cellulose nitrate, for example (used as an emulsifying agent for dispersing water in a mixture of amyl acetate and benzene), in the film should be in equilibrium with the amount in solution. "An ideal emulsifying film," according to these investigators, should be elastic and tough and change but little on ageing. Such a film will be gelatinous and swollen on the oil side because of the peptizing action. On the "water" side the cellulose nitrate will be coagulated and "wetted" somewhat by the "water" phase. Visible concentration films of cellulose were actually observed around large drops of water emulsified in an amyl acetate/benzene system. Newman¹⁸⁰ also assumed that a hydrophilic or a hydrophobic colloid, in order to be a good emulsifying agent, must be able to form a coherent film around the internal phase. He states that for a permanent emulsion the film around the globules of the emulsified phase must not age very much.

Sheppard²⁴² obtained photomicrographs of certain aged granular systems of paraffin oil in water with saponin as an emulsifying agent, and of

nitrobenzene in aqueous sulfuric and hydrochloric acids, with tannin, dextrin, gum arabic and lampblack as emulsifiers. At higher magnification (100 times), the globules of the disperse phase appeared to be covered with semi-elastic membranes consisting of, or containing, small globules. Seifriz²³⁵ has published interesting pictures of interfacial films as developed in hydrocarbon oil emulsions stabilized by casein (Fig. 7). It is generally agreed that emulsifiers form interfacial membranes (Langmuir, Harkins and Adam). A microscopic examination of a petroleum emulsion, according to Wright,^{293a} at times shows water globules with a withered or skin-like membrane. The adsorbed films stabilizing emulsion droplets are not always of sufficient thickness to be visible under a microscope. It is true that, in many oil emulsions to which a substance has been added as a stabilizing agent the membranes surrounding the dispersed liquid particles are definite morphological structures, which at times are visible under a microscope.

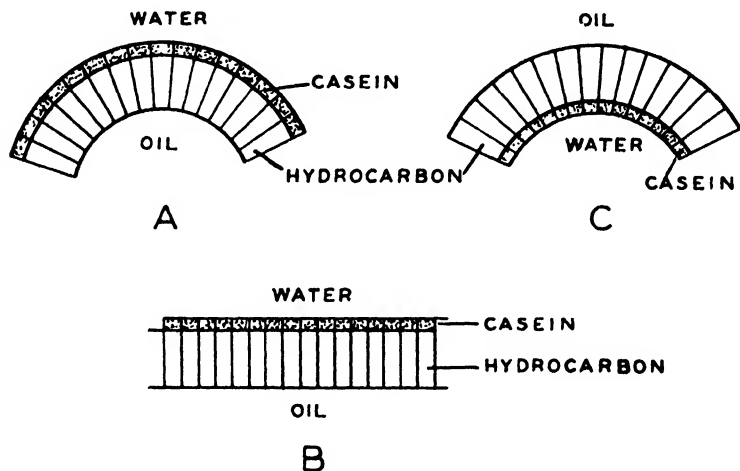


FIG. 7. A. The petroleum oil is of light weight (specific gravity below 0.828) and the emulsion is an oil-in-water one. B. The petroleum oil is of medium weight (specific gravity 0.828 to 0.857) and cannot be emulsified. C. The petroleum oil is of heavy weight (specific gravity above 0.857) and forms a water-in-oil emulsion.

Briggs^{29,30} emphasized the point of view that apparently soluble emulsifiers are in colloidal suspension in the external phase of the emulsion and therefore constitute a third phase in the system, exactly as a solid emulsifier is seen to constitute a third phase in such systems. That emulsifying agents may be in true solution was amply proved by Holmes and Williams.¹⁸¹ The globules of liquid in all ordinary emulsions are invariably coated with some kind of film or pellicle which tends to prevent coalescence; and this film is present whether the emulsifier is apparently soluble or consists of a finely divided solid. Thus, in view of most of the experimental evidence, it seems safe to assume that the presence of a film of emulsifying agent is essential to the existence of all

ordinary emulsions.^{235, 236} The interfacial film between the two phases of an oil-in-water emulsion may be, because of refraction, a definite structure visible in a microscope; or the conditions may be such that oil and water are apparently miscible. When an emulsion passes through the transition stage from one type to the other during inversion, the interfacial tension is reduced to a minimum, as would be expected. Theoretically, there should be a point at which the surface tension between oil and water is zero.

Adsorption phenomena, as applied to petroleum emulsions, are discussed by Gurwitsch,⁹² who states that "In petroleum oils and most petroleum distillates we have to do with solutions of resinous and similar hydrocarbons. These compounds reduce the surface tension of the oily constituents at a limiting surface of water or solution of salt very considerably. Therefore, at the oil/water surface a more or less considerable concentration of resinous and similar substances must always take place. This same phenomenon plays the principal part in the formation of petroleum emulsions. In this case the surface layer of this liquid must become a more concentrated solution of the dissolved substance, and by this means a thin film may be formed on the limiting surface of the drop of sufficient stability to withstand the disruptive action of the surface tension, and to prevent fusion of the drops." Such film-forming substances are found in petroleum and petroleum products in the asphaltic and resinous compounds on one hand, and in soaps of naphthenic acids on the other hand. Gurwitsch expects, according to Gibbs' theory, a concentration of asphaltic and resinous substances, as well as of naphthenic soaps, at the limiting surfaces of petroleum and petroleum products in water. This may be proved to be the case by direct tests such as, for instance, the agitation of a dilute solution of petroleum resins in gasoline with water. After agitation has ceased, there is a considerable layer of an emulsion of honeycomb structure, consisting principally of angular, relatively large cells filled with water, their walls made up of thin films of oil between the gasoline solution and the water. That these films possess considerable stability is shown by the fact that they sustain, without breaking, a small piece of glass thrown on them; and ragged fragments of these films are seen hanging in the water. Such behavior of emulsion films suggests that they do not consist of the original gasoline solution, but are concentrations of the solid, resinous substances. This may be proved by analyses of the gasoline solution before and after agitation with water. In one experiment, for instance, the resin content of the solution fell from 1.015 to 0.998 per cent after agitation with water, and in another from 1.647 to 1.628 per cent. The fact that various petroleum products form different resin films on agitation with water is also of great interest. If, for instance, a one-per cent solution of petroleum resin in kerosene is used instead of a gasoline solution, the film has much less strength and stability than in the other case. Still weaker films are formed by a one-per cent solution of spindle oil. The honeycomb emulsion, initially formed after shaking, is destroyed quite rapidly on stand-

ing, because the film walls of the cells collapse and finally only a thin layer of emulsion is left, consisting of small drops of water floating in oil. The reason for this different behavior seems to be that, according to Gibbs' theory, the more the dissolved substance concentrates in the boundary layer the more the surface tension of the oil is depressed. The depressing influence of the petroleum resins on the surface tension between water and gasoline is considerably stronger than that between water and kerosene, and the latter is stronger than in the case of water and spindle oil as shown in Table 10.

Table 10. Surface Tension (dynes/cm) in Contact with Water.
(Gurwitsch)

	Pure	0.01% Resin	Diff.	0.5% Resin	Diff.	2.0% Resin	Diff.
Gasoline	48.1	35.5	12.6	26.4	9.1	23.0	4.3
Kerosene	42.4	38.6	3.8	39.2	1.4
Spindle oil	28.9	26.9	2.0	26.0	0.9

In view of these figures, it is to be expected that the solid, resinous substances will be much more concentrated in the boundary layer between the gasoline solution and water than between kerosene or spindle oil and water; therefore the films in the first case will possess the greatest stability and the least in the last case. The reason for the various strengths of films is assumed to be the differences in surface tension ratios and not any variation in other physical characteristics, such as the viscosities of the respective liquids.

More or less resistant films may be formed by the concentration of naphthenic soaps at the boundary surface between oil and water. These films may also possess varying degrees of stability and form various kinds of emulsions—slimy, honeycomb, creamy, or milky, according to circumstance. It has been shown directly by Briggs³⁰ for an emulsion of benzene in an aqueous solution of sodium oleate that a concentration of soaps really occurs in such films. Emulsions of this kind may also be formed when soaps are absent either in the oil or in the water phase, and when free naphthenic acids are present in the oil, and alkaline salts in the water. By their interaction, small quantities are sufficient to form films upon agitation of the two liquids, thus forming emulsions. Gurwitsch proved by the following experiment that such a process is actually possible. A Bibi-Eibat petroleum oil, of specific gravity 0.880 and an acid content of 0.018 per cent of sulfur trioxide, had a surface tension of 26.0 when in contact with distilled water; but when in contact with sea water which had been evaporated until its specific gravity was 1.082, it had a surface tension of only 5.5. Upon vigorously agitating the two liquids together, a thick, stable emulsion was formed that appeared to be very similar to the Bibi-Eibat naphtha emulsion discussed below. This was destroyed by a small amount of naphthenic acid, but not by heat. This natural emulsion often contains up to 90 per cent of water. The presence of naphthenic soaps in these films may also be shown by direct

analysis. After the destruction of the films with ether and the extraction of the separated agglomerate with petroleum spirit, Gurwitsch obtained 0.0078 g of a solid substance from 500 g of emulsion in which naphthenic acids could be detected by Charitschkoff's copper reaction, and traces of lime by incineration.

Lange¹⁴¹ classified emulsifiers into ion-exchanging, chemically acting, and physically acting protective colloids called stabilizers, the latter characterized by their ability to form hydrates (silicic acid sol), to swell in water (gums, glues and starches) and, because they are less viscous liquids, to form films. According to Lange, true emulsifiers contain in their molecule salt-forming groups such as OH, COOH, SO₃H, NH₂ and CO which, like the auxochrome groups of the coal-tar dyes, induce solubility of the emulsifier. There is a possibility that an emulsifier may, at the same time, be a stabilizer, depending upon whether the solubility or the wettability of the substance forming the interfacial film dominates.

Casein as a salt-forming albumin, with which alkali or calcium salts form viscous, glutinous solutions, acts as an emulsifier, producing dense foams. Gum arabic of the carbohydrate class shows, on the contrary, more protective properties; and its ability to emulsify, *e.g.*, almond oil is only 1/10-1/20 of that of potassium oleate as well as of saponin solution.¹⁴¹ As the ability of an emulsifying substance to split off ions decreases, its suitability as a stabilizer increases. The difference in the action of an emulsifier and a stabilizer is shown by Lange in the following experiment: when a vegetable or an animal oil (a mineral oil proved to be less suitable) is poured slowly down the wall of a container into a one-per cent potassium soap solution, and a visible separation of oil globules into the surrounding soap medium takes place; replacing this by a solution of lecithin or gum arabic, which are typical stabilizers, no movement is observed, and the oil flows in and spreads out on the aqueous solution. A vigorous stirring, however, may cause the oil to emulsify in both cases. The emulsion formed with gum arabic is inanimate, but is sustained by viscosity, nevertheless, as a very stable pseudo-emulsion (Refer to Spiro Festschr. f. Madelung 1916, 64).

Sherrick²⁴⁴ states that substances which function as emulsifiers, by collecting at the interface between the two liquids to form protective films for the disperse phase, vary in nature. It has been claimed that ions adsorbed on the surface of liquid particles may serve as emulsifiers, and Ellis has prepared emulsions which owe their stability to ion adsorption. In working with phenol/water mixtures, Ellis noticed that the emulsion formed on separation of the second liquid layer from a saturated solution of phenol in water persisted for hours. To Ellis, it seemed not unlikely that any slight stability which this phenol-in-water emulsion may have had was due to hydrogen-ion adsorption. It is probable, however, according to Sherrick, that in the formation of emulsions of relatively high concentration, *i.e.*, about 50 per cent or more of the disperse phase, an emulsifier is necessary which will form a relatively tough and elastic film by collecting at the interface. But it is rather difficult to

believe that emulsions containing 10 to 60 per cent of the disperse phase owe their stability to ion adsorption alone. Even though Ellis prepared emulsions stabilized by ion adsorption, they were extremely dilute and only of the oil-in-water type. It seems improbable that ions could stabilize a water-in-oil emulsion even though they might be effective for an emulsion of the opposite type. As mentioned above, it is not only emulsifying agents which are soluble in the external phase of an emulsion or colloiddally dispersed in it that produce and stabilize emulsion systems but also, as first pointed out by Pickering, emulsifiers in the form of finely divided solids, insoluble in either of the phases.

Pickering¹⁹² assumed that no explanation of emulsification would be readily accepted unless it could be applied equally to cases where the emulsifier is either a liquid or a solid. The view that emulsification depends solely on the minuteness of the solid particles must be modified, so as to apply only to such solids as are wetted more readily by water than by oil; otherwise there is no emulsification. According to Pickering, liquid emulsifiers are substances which, under the existing conditions, partly separate from the solution and yet yield sufficient solid particles to form a pellicle around the oil globules. All liquid emulsifiers are distinguished, as far as it is known, by a feeble affinity for water. In many cases liquids are, or contain, protein substances which, as Ramsden has shown, form a skin of solid matter at any boundary between the solution and another fluid, whether liquid or gaseous. In other cases, the deposition of some particles of the solid would result from its insolubility in the oil (paraffin). The water in the neighborhood of an oil globule, such as paraffin, would become impregnated with paraffin and the dissolved substance, having little affinity for water, would be thrown out of solution. In this way, each oil globule would adsorb the solid particles necessary for its emulsification. These particles would, no doubt, redissolve, while others in their turn would be deposited. Emulsions prepared with insoluble emulsifying substances are similar to those prepared with soluble substances except that they never appear to break down spontaneously. Large amounts of a solid substance not completely dispersed cause phenomena similar to that in an emulsion in which the oil phase adheres to the solid phase, but separates again on dilution with water. Solid particles used as emulsifiers for an oil-in-water emulsion, for example, must not have a tendency to agglomerate, but must have some kind of adsorption at the oil/water interface, and be more readily wetted by water than by oil.

Pickering prepared emulsions of a petroleum oil in water with the aid of so-called basic copper sulfate and other finely divided precipitated solids. From lime, plaster of paris, chalk, silica and alumina, emulsions of fair stability were obtained, which he termed "quasi-emulsions." Pickering showed that droplets of oil were prevented from coalescing by being coated with a pellicle of the finely divided solid material. In all his emulsions, however, oil was the disperse phase; experiments with emulsions in which water was suspended in oil were not completed.

According to Pickering's definition of the formation and the existence of an emulsion produced by solid emulsifiers, one should obtain an emulsion of water in oil if the insoluble particles are more readily wetted by oil than by water. This suggestion was confirmed by Schlaepfer²³³ and by Moore,¹⁷⁴ who emulsified water and ammonium chloride solutions in kerosene with carbon black (gas black or soot extracted with hot benzene). The emulsion obtained with 70 cc of water, 30 cc of kerosene and 1 g of carbon was found to mix freely with kerosene, but not with water. Under the microscope it was observed that the water droplets were covered with a dark brown skin of adsorbed particles of carbon, those particles not adsorbed forming aggregates in the kerosene phase. It was also noticed that the order in which the ingredients were added made no difference in the final result. In no case was it found possible to prepare an emulsion of oil in water by using carbon.

Carron oil, a mixture of lime water and linseed or rape oil, is another example of a water-in-oil emulsion. Moore states that highly calcined lampblack and calcined petroleum coke are not suitable for emulsification, probably because of their inability to form a coherent film in the Bancroft¹² "dinêric interface." The material used by Moore was commercial lampblack prepared by incomplete combustion of creosote oils. The results obtained with mixtures of lampblack and kerosene with ammonium chloride solution or water are in striking contrast to the behavior of lampblack with water, kerosene, or ammonium chloride solution alone. This crude lampblack, when shaken with water or ammonium chloride, rises to the surface of the liquid, the oil content in all probability preventing wetting. When shaken with water, purified lampblack forms a suspension. With kerosene, both crude and purified lampblack sink to the bottom. With a large quantity of lampblack having a large surface, smaller emulsified droplets of water are obtained in kerosene than when less lampblack is used. Water wets crude lampblack less readily than purified lampblack, the oils of which have been removed by benzene extraction. Ammonium chloride solution at normal concentration wets crude lampblack more readily than purified. Water wets purified lampblack more readily than ammonium chloride solution, the reverse being true of crude lampblack.

Bechhold, Dede and Reiner¹⁶ worked with water-in-benzene and water-in-paraffin oil emulsions using clay, zinc dust, yeast, etc., as emulsifiers. These investigators pointed out that emulsification with solid powders depends: (1) on the size of the particles (the smaller the grain the better the emulsification, until an optimum is reached beyond which smaller grains have inferior emulsifying properties); (2) on the amount of powder used as an emulsifier; and (3) on emulsifying promoters, which are soluble in one or both phases. As an example, they mention the water/pure benzene system with clay powder as an emulsifier from which an emulsion may be obtained after the addition of a few drops of pyridine, acetic acid, alcohol, sodium hydroxide, or sodium nitrate. Electrolytes, non-electrolytes, acids, bases, and salts are all agents promoting emulsifi-

cation. The mechanism of action of solid emulsifiers is believed to depend upon the wetting ability of the powder by the liquid components present, which is also influenced by the promoting agents. Scarlett, Morgan and Hildebrand²³¹ investigated the contact angle of emulsions of zinc, copper and glass powder in benzene, iron pyrites in toluene, and carbon and mercuric iodide in water by photomicrography.

Briggs³¹ indicated that a finely divided solid may serve as an emulsifier only if it has the power to separate out or concentrate at the interface between the two liquid phases of an emulsion system. This interfacial film must also be sufficiently elastic and continuous, and the particles must be extremely minute. Among solid emulsifiers, carbon black is known to emulsify water in oil, while finely divided silica emulsifiers are used for oil in water. Briggs also found that if the finely divided solid forms a stable suspension in one of the liquids, it may be necessary to add a weak flocculating agent before a satisfactory emulsion can be produced (a powerful flocculating agent will actually prevent emulsification).

Emulsions stabilized by solid particles are encountered in oil-field work. Finely divided clays are usually the emulsifying agents. Gurwitsch⁹² states that if a test-tube is partially filled with oil and water and fine sand is added, a portion of the sand adheres to the boundary surface of oil and water, although in water, without the addition of oil, the sand sinks to the bottom. In this way a more or less consistent and very stable emulsion is formed. Similarly, "naphtha" emulsions also occur naturally as, for example, those described by Wischetravski²⁸⁸ at Kale near Baku, as well as the Roumanian "Bososunga" investigated by Stanzs. Under the microscope it is clearly seen that these emulsions consist of many minute droplets of oil, irregular in shape, suspended in water, and covered on their surfaces with minute grains of sand. Since these sand films are relatively stable, the emulsions are also highly stable. Gurwitsch attributes the formation of these emulsions to the effects of surface tension at the liquid/solid interface.

Finkle, Draper and Hildebrand,⁷⁰ discussing the action of solid particles in stabilizing emulsions, state: "It is obvious first that the powder must collect at the interface in order to be effective, and second, that the type of emulsion produced by a solid powder is determined by the angle of contact at the interface with the solid. In order for the powder to remain in the interface the angle must be finite and, unless the angle is 90°, the interface will be either on one side or on the other side of the points of contact of the particles, its surface tension causing the film to be concave on that side. If there are enough solid particles to fill the interface, the tendency of the interface to contract will cause it to bend in the direction of the more poorly wetting liquid, which makes it easy for the latter to become the disperse phase." The solid,^{266, 267} in order to behave in this way, must be easily dispersed in the outer liquid, its particles tending not to agglomerate therein or to stick together when serving as a protective coating for the emulsified droplets. One should, there-

fore, be able to predict whether or not a given solid powder can stabilize an emulsion, and also which liquid will become the disperse phase, by noting the angle of contact with the solid at the interface. The theory of capillarity created chiefly by Laplace (*Traité de Mécanique céleste*, 1807), and also by Gauss, gives the following expression for the contact angle (wetting) derived from the conditions under which the equilibrium of forces act upon a solid (the three interfacial tensions) (Fig. 8):

$$\cos \alpha = \frac{\sigma_{0,s} - \sigma_{w,s}}{\sigma_{w,o}}$$

where $\sigma_{w,o}$ is the interfacial tension at the water/oil interface; $\sigma_{o,s}$ the interfacial tension at the oil/solid interface, and $\sigma_{w,s}$ the interfacial ten-

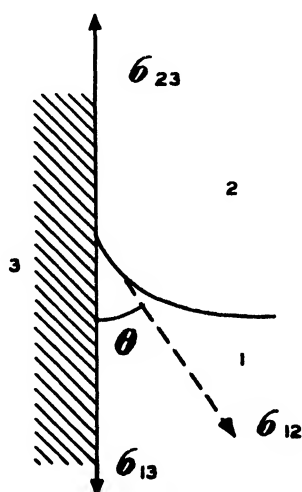


FIG. 8.

sion at the water/solid interface. If the angles of contact between liquids and insoluble solids were known, it would be possible to predict which of the two liquids would be the internal phase in an emulsion with a given insoluble powder.

In the disposition of a solid in the oil/water interface, three cases may be differentiated: (1) the solid is immersed in the water phase; (2) the solid is immersed in the oil phase; and (3) the solid is distributed in the "dimeric interface." Expressed in terms of interfacial tensions, the corresponding three cases are:

- (1) $\sigma_{s,o} > \sigma_{s,w} + \sigma_{w,o}$
- (2) $\sigma_{s,w} > \sigma_{s,o} + \sigma_{w,o}$
- (3) $\sigma_{w,o} > \sigma_{s,o} - \sigma_{s,w}$.

One of the liquids exhibits preferential wetting of the solid and the equilibrium state is: $\sigma_{s,o} - \sigma_{s,w} = \sigma_{w,o} \cos \alpha$. If $\sigma_{s,w} < \sigma_{s,o}$, then $\cos \alpha$ is

positive and α is $< 90^\circ$, and the greater portion of the solid is surrounded by water; if $\sigma_{s,o} < \sigma_{s,w}$, then $\cos \alpha$ is negative and α is $> 90^\circ$, i.e., the major part of the solid is surrounded by the oil phase.

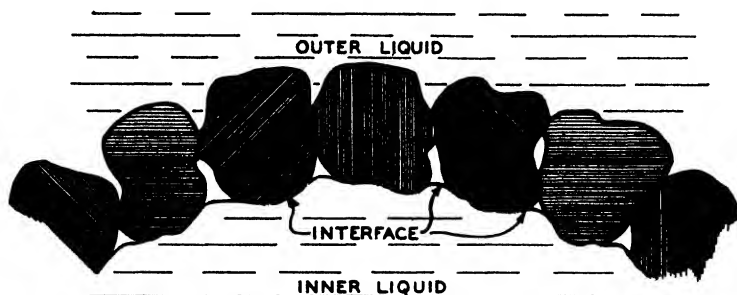


FIG. 9. Particles of a Finely Divided Solid Acting as an Emulsifying Agent.

Gibbs^{84,90} presented the mechanism of emulsification by means of solid agents in the following manner: "When the liquid molecules and those of the solid surface attract one another, wetting occurs and the liquid spreads to an extent which is determined by the spreading coefficient and which is indicated by the contact angle which the surface of the liquid finally makes with the solid surface. When two liquids rest upon a solid surface in relation to which they have different spreading coefficients or wetting power, one liquid is pulled towards the solid surface with more force than the other. They will spread until their advancing

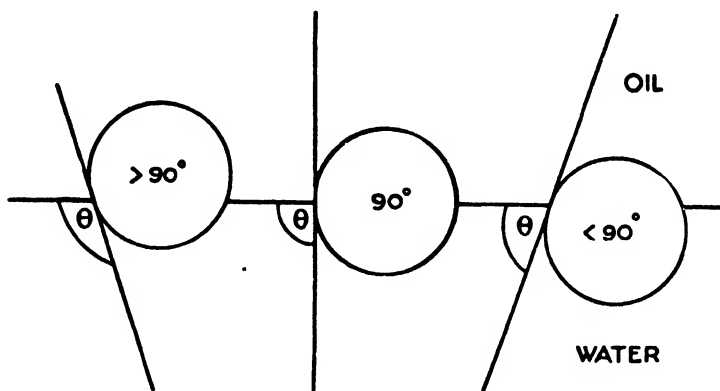


FIG. 10. Possible Arrangements of a Solid Emulsifying Agent at an Oil/Water Interface.

edges meet to form a liquid/liquid interface which will be inclined to the solid surface at an angle, the size of which will be determined by the balance between the three interfacial tensions liquid A/liquid B, liquid A/solid, liquid B/solid. The liquid/liquid interface will be inclined in the direction of the liquid which possesses the smaller spreading power."

The study of coherent films formed around the droplets in emulsions stabilized by solid particles has attracted the attention of investigators in the field of emulsions to the study of the exact nature of the films to be found in emulsions stabilized by soluble emulsifiers. In a number of papers the question as to whether these films are not also of the nature of solids has been raised. Pointing to the difficulties encountered in explaining emulsion formation, Pickering^{193, 194} remarks: "We may ask ourselves whether the emulsification of oil in soap solution or in other similar liquids may not be explained more satisfactorily by applying the same principles which have been found in the case of emulsification by solid particles." We have already quoted the statement of Gurwitsch that the behavior of emulsion films strongly suggests that they do not consist of the original benzene solution, but are concentrations of the solid resinous substances. In the emulsions studied by Ramsden,^{211, 212, 214} an actual solid membrane separated out at the liquid/liquid interface.

The experimenters on emulsions seem to be of the opinion that if an emulsion becomes permanently stable, the interfacial film must assume the nature of a plastic solid rather than of a viscous liquid. The distinction, as pointed out by Bingham,²⁶ is that a viscous liquid will be deformed by a force of any magnitude, while a plastic solid will flow if subjected to large shearing forces, but is able to resist small forces indefinitely without any change taking place. The adsorbed layer at the interface of an emulsion must always withstand forces, notably interfacial tension, which tend to cause coalescence. Low though this tension may be and high as the viscosity opposing it may be, the interfacial layer would give way in the end if it had the properties of a liquid, whereas it could exist indefinitely if it were a plastic solid.

Wilson and Ries²⁸⁷ made a careful investigation of the nature of adsorbed films at the free surfaces of liquids and at interfaces; they found definite evidence of the formation of plastic solid films at the free surfaces, particularly in bubbles. The failure of some solutions with low surface tension to give stable bubbles was attributed to the fact that they formed only fluid films. There was evidence of the formation of similar plastic solid films in the case of some liquid/liquid interfacial films where a substance which is a good emulsifying agent, such as saponin, was present in one phase. This would make it probable that such solid films are formed during emulsification. It follows from the above that investigators, who paid special attention to the adsorption factor of the emulsifier at the interface of the two immiscible liquids forming the emulsion system, chiefly discussed the question of the character of the interfacial layer. They considered the third substance, added in order to produce emulsification, as a pellicle around the oil globules, as a coherent or plastic film, as a membrane or a film sometimes even visible in the microscope, or as some kind of a skin easily formed, as by peptone and saponin when used as emulsifiers. Later, Pickering's idea led to the possibility of using not only soluble or colloiddally dispersed substances as emulsifiers, but solids as well.

Roberts,²²⁴ in his new theory of emulsions, considers that adsorption at the interface originates, not in an adhesive action of the latter, but in the mass of particles which are forced to the surface and are least attracted by the liquid, that is, those for which the relation of charge to mass is the smallest. This relationship is much smaller for polar molecules than for ions; therefore the former are preferentially adsorbed. In the formation of a new boundary the ions, because of their great mobility, occupy it first. However, in the equilibrium state, there is a definite relationship between ions and molecules in the adsorption layer determined by the relative concentrations, polarities, mobilities, etc. of the ions and molecules. The primary adsorption layer on the oil side is considered to be monomolecular, and remains undisturbed in streaming potential and cataphoresis measurements, while the adjacent diffuse atmosphere of ions and molecules is mobile.

Identification of the films produced by soluble substances and solid materials has been attempted. The mechanism of emulsification was formulated according to the wettability of emulsifying substances and their respective affinities for the continuous phase. In most cases, an invisible adsorption layer in the interface must be considered, so that there is no possibility of investigating the film directly; but there are indirect methods of judging the interface layer or film. By the use of these indirect methods, it is possible to determine how large the area of the film is, how fast the film is formed by emulsification, to what kind of changes it is subjected, and whether it reaches a certain equilibrium with time. Therefore, the dynamic as well as the static behavior of the film should be thoroughly investigated. When the film is spoken of as protecting the globules of an emulsion from coalescence or giving permanence to an emulsion, the question arises as to the actual thickness of this film at the interface. Is the stabilization membrane monomolecular or polymolecular in thickness? Bancroft¹³ and Griffin,⁸⁸ were the first to offer a probable answer to this question. van der Meulen and Riemann,²⁷² McBain,¹⁰⁴ Finkle, Draper and Hildebrand,⁷¹ Langmuir,¹⁴³ Harkins and Beeman,¹⁰⁴ Harkins and Berkman,²² and Fischer and Harkins⁷⁴ made further contributions in this field.

Langmuir^{143,144} and Harkins¹⁰⁰ stated that in emulsions in which soap is the emulsifying agent the oil droplets are surrounded by a film of soap one molecule thick. Griffin,⁸⁸ working with emulsions of kerosene oil in water, and using palmitic, stearic, and oleic soaps as emulsifiers, determined the average area of interface covered by each molecule of soap. If an emulsion consists of droplets of oil, each surrounded by a film of soap one molecule thick and the whole surrounded by a soap solution containing the unadsorbed soap, it might be possible to determine the soap extracted from the water solution in the formation of the emulsion.

Briggs³⁰ made titrations which showed that soap was removed, but did not obtain absolute measurements, his results being only comparative. Griffin⁸⁸ assumed that the average area of interface covered by each molecule of soap can be calculated from a comparison of the amount of

soap removed by each cubic centimeter of kerosene with the area of interface formed by the same amount. For example, when kerosene is emulsified by shaking in fairly dilute sodium oleate solution and is then allowed to stand, oil droplets cream out at the top, leaving a clear or nearly clear aqueous soap solution at the bottom. If this soap solution is analyzed before and after emulsification of the kerosene, the difference in the quantity of soap will be that taken up by the kerosene. Griffin calculated the area of interface as follows: An oil-in-water emulsion with soap as the emulsifier contains droplets of various sizes which are assigned to various classes whose radii, expressed in centimeters, are r_1 , r_2 , r_3 , and r_4 , respectively. The number of drops, X_1 of radius r_1 (measured), is calculated by using a special micro-projection apparatus. Those with radius r_2 are denoted by X_2 ; those with radius r_3 by X_3 , and so on. Then the area of interface associated with each cubic centimeter of kerosene is the sum of the areas of these droplets divided by the sum of their volume, or:

$$\frac{3(X_1r_1^2 + X_2r_2^2 + X_3r_3^2 + \dots)}{(X_1r_1^3 + X_2r_2^3 + X_3r_3^3 + \dots)}$$

The area of interface associated with one cubic centimeter of kerosene divided by the number of molecules of soap removed gives the area of interface formed for each molecule of soap removed. Griffin found the interfacial area formed per cubic centimeter of kerosene to be equal to 7.45×10^{-3} sq cm and the area for each molecule of sodium oleate removed from solution, 44×10^{-16} sq cm. The result obtained bears out the assumption that the areas measured should be the same or somewhat greater than those measured by Langmuir for the corresponding fatty acids in surface films. The average value for the soaps as determined by this method are 48, 27, and 30×10^{-16} for sodium oleate, potassium stearate, and potassium palmitate, respectively, and those for the corresponding fatty acids as determined by Langmuir, 46, 22, and 21×10^{-16} . Griffin assumed that the values obtained indicate that the film formed at the interface must be one molecule thick, and that the explanation is the formation of a film of heavily hydrated soap of constant thickness at the interface. As these films were obtained from solutions of widely varying concentrations, and as the hydration of soap in a precipitate depends on the concentration of the solution from which it is precipitated, Griffin concluded that this assumption is untenable. He mentions the fact that an emulsion, like kerosene emulsified with a solution of soap, is stable when a monomolecular film is formed, but, when there is insufficient soap to form a monomolecular film, the emulsion is not stable. If excess soap is present, it remains dissolved in water. Griffin, who actually was the first to measure the thickness of the protective film in an emulsion, did not overlook the fact that, when kerosene is emulsified with a neutral soap solution, the soap is partially hydrolyzed and some of the fatty acid dissolved in the kerosene. He thought that the hydrolysis might be prevented, or at least reduced to a negligible amount, by the addition of free alkali. He used 0.01 molal sodium hydroxide to make the concentration

of the undissociated fatty acid in the soap solution so small that the quantity taken into solution by kerosene was negligible.

van der Meulen and Riemann²⁷² independently started their work about the same time as Griffin. They used quite a different method from that used by Griffin for determining the area of interface in an emulsion system. The average area of interface covered by a molecule of sodium ricinoleate in an emulsion of a solution of phenol in toluene dispersed in water was determined. The content of soap in the interfacial film was determined by analysis as follows: If A is the acid necessary to neutralize the lower fraction, B the whole dilute emulsion, and C the fraction of external phase in the whole dilute emulsion as computed from the composition of the emulsion, then the percentage of soap in the film equals $\frac{B-AC}{B} \times 100$. The diameter of the globules was determined by using two independent methods. One was to count the globules in a given volume, composition of the emulsion being known. The average volume of the globules and hence the average diameter could be calculated. The second method consisted of fixing the globules on a slide under a microscope and measuring them with a filar micrometer eye-piece; the average area values are recorded in Table 11.

Table 11

Average area per molecule
of soap in A²

39.2
44.2
66.2
105.6
43.6
48.8

From the tabulated results, it is evident that the average area covered per molecule varies with the concentration of the soap in the external phase of the concentrated emulsion. They concluded, therefore, that the area per molecule is a function of the concentration of soap in the external phase in the case of concentrated emulsions, and that the area covered in the various cases does not disprove the assumption that there is a monomolecular soap film at the interface. It must be noted, however, that these investigators did not consider the hydrolysis of the soap sufficiently important for the addition of 10 per cent excess alkali which, according to Griffin, prevented hydrolysis. As they state, the addition of alkali did not cause an appreciable difference in the average area per molecule.

Harkins and Beeman,¹⁰⁴ in their work "On the Oriented Wedge Theory of Emulsions," attempted to determine the area of the interfacial film and also its thickness, but they did not reach a conclusion on this question. In order to draw conclusions on the actual thickness of the interfacial film, it seemed necessary to carry out a systematic study of the problem,

as well as an investigation of the influence of various factors on the film formed at the interface. S. Berkman and Harkins,²² taking into consideration Griffin's viewpoint, found that calculations of the thickness of the interfacial film can be made by obtaining the number distribution of sizes of the emulsions; a special micro-projection system to insure accuracy of the method was used. For accuracy of analysis, an exact separation of the clear aqueous layer from the oil layer to be analyzed is necessary. Accurate separation of layers without losing the least amount of the components and without disturbing the natural equilibrium of the system on standing is performed as follows. After standing in a graduate fitted with a glass stopper for the desired time the emulsion exhibits distinct, separate layers. By using tubes drawn at one end to capillaries of various diameters, the upper layer is suctioned off by a pump. The speed of suction is controlled by inserted pinch and stop cocks; in addition to this, a slow rotating movement is given to the suction capillary near the walls of the graduate so that the layer is suctioned off slowly and uniformly. Previous investigators used the centrifugal method of separation, overlooking the fact that when an emulsion stands for a time an equilibrium state is reached. When an emulsion is centrifuged after it has stood two or three days, its natural equilibrium is disturbed; this necessitates an investigation to determine the permanence of the system. With this fact in mind, S. Berkman and Harkins worked under conditions of static equilibrium and not with emulsions having a dynamic equilibrium.

The emulsion systems on which the investigation was carried out were octane/water and Stanolax/water emulsions, with sodium oleate as the emulsifier. The amount of soap adsorbed, forming a film between the oil and water, was determined for these systems with various concentrations of the emulsifier, and the changes occurring in the film were observed, *e.g.*, its change in thickness with time, when the emulsion had not yet attained its final equilibrium. Two types of stability of an emulsion were distinguished, namely, initial stability (thickness of a film measured during the first few days after preparation), and static stability of an old emulsion (months and years). The results obtained indicate that the area of interface for the octane emulsions with various concentrations of soap as emulsifier changes with time, usually showing a minimum 7 to 12 days after preparation and then gradually reaching a definite magnitude. The absolute area of interface does not change much with time and does not seem to depend particularly upon the concentration of the emulsifier. When static stability is reached, the area of interface for various concentrations of soap is about the same. The area of interface for Stanolax emulsions is greater than for octane emulsions. The area of interface in the case of Stanolax emulsions also shows a lower minimum in the first period of ageing of the emulsion and a subsequent increase when the emulsion reaches static stability.

Stanolax emulsions do not form interfacial films as easily or as quickly at high concentrations of the emulsifier as octane emulsions, because of

the viscosity of the heavy paraffin oil and the changed conditions in diffusion. The amount of soap adsorbed at the interface, as found by analysis, is of an order of magnitude which would be expected for emulsions with various concentrations of the emulsifier. This indicates, in all probability, that an emulsion of static stability has a soap film of a definite thickness in the interface. The thickness of the adsorbed layer, corresponding to the film, can be calculated from the area of interface by using the distribution curves of sizes and from the amount of acid or soap removed, as determined by analysis. The area of the oleic acid molecule calculated theoretically by Langmuir is 20 \AA^2 . A comparison of the experimentally determined area with the theoretical area per molecule gives the thickness of the film expressed in number of molecules. The results obtained by S. Berkman and Harkins indicate that static stability corresponds to the presence of a protective film one molecule thick. But the thickness of the film calculated for an emulsion having a high concentration of emulsifier, as well as for emulsions measured three to four years after their preparation, was found to decline from this value. This does not mean that the stable state of an emulsion should correspond to a protective film one molecule more or less in thickness. Rather, it seems to indicate that hydrolysis of the emulsifying soap takes place, and it is considered possible that a part of the oleic acid removed goes into the oil and is absorbed by it, and is not adsorbed at the interface. Therefore, what is found as the amount adsorbed at the interface is actually less than what would be obtained if hydrolysis had not occurred. The fact that a smaller amount of adsorbed acid or soap was determined accounts for the smaller result for the thickness of the film. S. Berkman and Harkins attempted to prove this idea experimentally.

A small excess of $0.01M$ sodium hydroxide was added to an emulsion of octane and water, using $0.1M$ sodium oleate as emulsifier; and the results obtained were in agreement with the above explanation. In this case the film was actually about one molecule thick, and the ageing of the emulsion did not greatly affect the absolute value of the area of the molecule. These results led to the conclusion that due consideration should be given to hydrolysis occurring in emulsions, and that future investigations should be carried out with the idea of determining the thickness of the interfacial film, bearing in mind the conditions influencing hydrolysis and its prevention.

Fischer and Harkins,⁷⁴ studying emulsions of a paraffin oil, observed that the maximum number of particles has a diameter of about one micron, whereas with benzene the maximum occurs with a smaller diameter. In plotting the area per cc against particle size, they found that the greatest contribution to the area is given by particles between 6 and 7 microns in the Finol emulsions and 1 and 2 microns in the benzene emulsions. The area per molecule of soap in the interfacial film lies in general between 24 and 38 \AA^2 . The area per molecule in a condensed monomolecular film of oleic acid at zero compression is about 20.5 \AA^2 . Therefore these areas correspond to an expanded monomolecular film of

oleic acid with an emulsion containing 0.02 mol of sodium oleate and 0.004 mol of sodium hydroxide (to prevent hydrolysis), the initial molecular area of the interfacial film corresponded to 44.5 \AA^2 which, on ageing, returned gradually to the value of 20 \AA^2 .

Serrallach, Jones and Owen^{239, 240} attempted to measure the strength of coherent films in the liquid/liquid interface between emulsifier solutions and various oils. Four groups of emulsifier/oil pairs could be differentiated with regard to constancy, decrease, and/or smaller or larger increase in the strength of the film. Saponin, tragacanth, triethanolamine, Irish moss, gelatin, sodium oleate and sodium glycocholate solutions were tested as emulsifiers. Oils used were olive, castor, mineral and cod liver. A modified de Noüy interfacial tensiometer, an instrument designed for the measurement of surface tension at the interface of two liquids, was used for measuring quantitatively the strength of the coherent interfacial film. When the film broke, the force per centimeter was read directly from the vernier on the torsion head. The experiments indicate that the efficiency of an emulsifier does not depend primarily on the strength of the films formed. The preliminary lowering of the interfacial tension and the rapidity of film formation are considered to be the main factors. Any later increase in the strength of the film will be favorable. A considerable lowering of the interfacial tension insures a small particle size, and quick film formation gives an early protection to the globules against coalescence.

Orientation of Molecules in the Adsorbed Interfacial Layer as an Explanation of Emulsion Stability and Other Emulsion Properties

According to the theory of molecular orientation, the molecules of two liquids at an interface arrange themselves so that their stronger polar portions, *i.e.*, the atomic group in each molecule which exerts the greatest electromagnetic force directed toward the interface, leave the less active portions of the molecules to form the actual surface. This is true only on the oil side of oil/water interfaces.²²⁴ In other words, the molecules arrange themselves at the surface so that the surface energy is at a minimum. The interfacial molecules assume such a position in order that the transition from one liquid phase to the other may occur with the least possible abruptness. If octyl alcohol is placed on water, the end of the molecule bearing the hydroxyl group turns toward the water, since the hydroxyl group is similar to water and is more soluble in it than the hydrocarbon group. This position makes the transition between phases less abrupt. Such an orientation is in accord with the general principle that, at a surface, the arrangement which gives the lowest free energy will be the most stable. Evidence showing that the extent of average orientation in a surface is sufficient to produce a noticeable effect in the characteristics of the surface region has been supplied by Harkins¹⁰⁰ and Langmuir.^{143, 144} Hardy,^{96, 97, 98} in 1912, was the first to suggest this idea. In connection with investigations on the water/benzene system, the question arises as to the distribution of a polar/nonpolar molecule of butyric

acid (Fig. 11). The solubility of this substance in polar water is due to the polar carboxyl group $\text{—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—O—H}$, and its solubility in nonpolar ben-

zene is due to the nonpolar alkyl group, $\text{CH}_3\text{CH}_2\text{CH}_2$. The solubility of butyric acid in the polar phase is decreased by its hydrocarbon chain and in the nonpolar phase by the carboxyl group. The thickness of a surface film formed in water gives excellent evidence in favor of orienta-

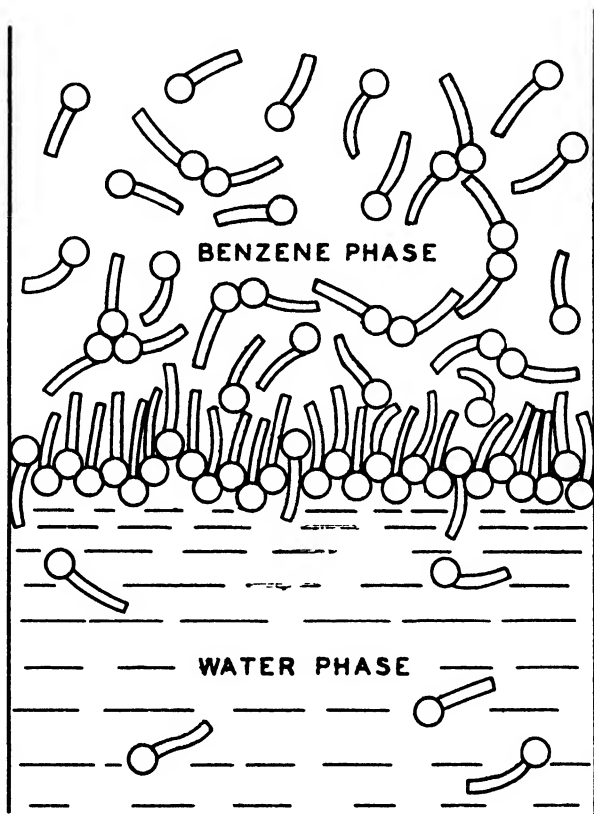


FIG. 11. Butyric Acid Distributed between Water, Benzene, and the Interface between the Two.

tion. For the proof of the direction of orientation, *i.e.*, whether the polar or the nonpolar end of a molecule, such as oleic acid, is uppermost, Harkins suggested comparing the works of adhesion and cohesion, and of energies of surface formation and vaporization. Orientation requires unsymmetrical molecules. In the case of molecules wholly symmetrical, there is no orientation. If a molecule increases its symmetry without a change in composition, theory indicates that its work of cohesion, W_c , increases and its work of adhesion, W_A , decreases. An increase in sym-

metry not only reduces the extent of orientation, but decreases the effect of orientation upon the surface energy.

In an emulsion a solute-emulsifying agent is usually present in one of two liquid phases. If a solute in any two-phase liquid system is a substance with a polar or active group, its electromagnetic field of force will cause the molecules at the interface to take up an oriented position in which each end of the molecule will be directed toward the phase which it closely resembles. According to the theory of Harkins and Langmuir, the emulsifying agent may be considered as acting like a bridge, or a link, drawing together the opposing surface molecules at the interface by attracting them one to another. It is well known that soaps are able to

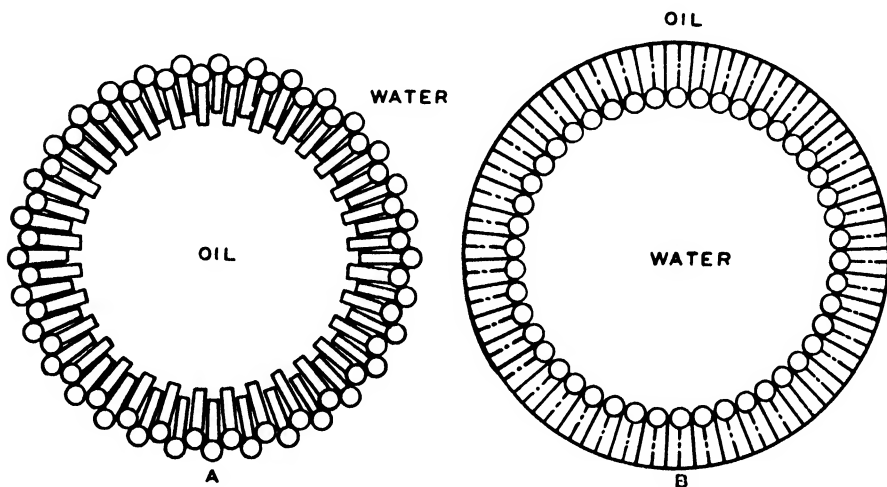


FIG. 12. Molecules of the polar-nonpolar type with polar ends weighted toward water. (a) Water outside. (b) Water inside, oil outside. This occurs when there are two hydrocarbon chains and COO^- groups attached to a single atom of a bivalent metal. If, however, there is only one hydrocarbon chain this may be taken to represent a drop of water surrounded by an octyl alcohol film floating in air, as described in the text. Both diagrams are highly conventionalized as the molecules in the film are undoubtedly moving with great rapidity.

emulsify mixtures of water and mineral oil. The molecules of soap, according to the orientation theory, tend to orient themselves at the interface so that the paraffin chain is in the oil, while the active COO^- -metal end is in the water. The length of the molecule opposes thermal agitation, tending to destroy regular arrangement in the case of smaller molecules. Harkins' drawings¹⁰² represent such a placement of soap molecules at the interface of oil-in-water and water-in-oil emulsions (Fig. 12).

The cohesive force of each liquid phase is diminished at the interface by the force of adhesion which is exerted upon the surface molecules of each liquid by appropriate portions of the molecules of the emulsifying agent. The result is a general reduction in interfacial tension. At the same time, the soap becomes adsorbed at the interface to form a pro-

TECTIVE film or membrane. Harkins has related orientation to a decrease in interfacial tension which is produced by most emulsifying agents. He states that if, at an interface, the transition from liquid *A* to liquid *B* is made by a saturated film of solute molecules which have one end like *A* and the other like *B*, the free surface energy, and therefore the interfacial tension, will be far less than when the two liquids are directly in contact.

Harkins, Davies and Clark¹⁰⁶ also pointed out that the stability of emulsion particles seems to be brought about by the orientation of molecules at the interface. For the emulsion particle to be stable, the molecules which make the transition from the interior of the drop to the dispersion medium, *i.e.*, the molecules of the film, should fit the curvature of the droplet. From this standpoint, the surface tension or interfacial tension of very small drops is a function of the curvature of the surface. These investigators mention the fact that the orientation of molecules at the interface between the dispersed particles and the dispersion medium is such that the molecules fit the curvature of the droplet and, at a definite droplet size, produce a stable system; the molecules in the curved surface need not necessarily be all of the same kind. If the molecules do not fit into the curved surface, the droplet will not be wholly stable and will either decrease or increase in size.

The validity of Harkins' theory relating to curvature at the interface and the shape and size of adsorbed molecules has been disputed. Roberts* believes that there is no relation whatever between the shape and size of a molecule and the curvature or the "equilibrium" size of emulsion droplets. He states that by comparing it with the sizes of molecules, even the smallest droplet visible in the microscope is enormous. For example, a droplet 10^{-5} cm in diameter has a surface area of about 3×10^{-10} sq cm, or 3×10^6 Å². It could, therefore, accommodate 5×10^4 molecules, each having a projected area of 60 Å². In other words, the equatorial circumference of such a droplet would be 3×10^3 Å. If the adsorbed molecules have a width of about 8 Å ($\sqrt{60}$ Å), about 400 could be placed around the equator, from which it appears that the angular displacement of the axes of adjacent molecules, normal to the interface, would be only about 0.9°, or about 54 minutes of arc. Furthermore, it has been repeatedly shown that the size of emulsion particles is a function of kind, duration, and intensity of agitation, and is independent of the shape or dimensions of the emulsifying agent.

Harkins assumed that the type of emulsion (oil-in-water or water-in-oil) formed depends upon the orientation and packing of the molecules of the emulsifier at the interface. In an emulsion of a hydrocarbon oil and water, the molecules of the emulsifying soap would be so oriented that the polar group, COONa, is in water and the hydrocarbon chain in oil. The adsorbed molecules will then be closely packed together at the interface, particularly if the concentration of soap in water is fairly high. He further states that if the cross-sectional area of the terminal

* Private communication.

atom of the polar group, in this case the metal atom, is greater than that of the hydrocarbon chain, then the water surface of the adsorbed film will necessarily be greater than the oil surface, i.e., the water will surround the oil and an oil-in-water emulsion is obtained. Conversely, if the cross-sectional area of the metal atom is less than that of the hydrocarbon chain, a water-in-oil emulsion is formed. Further, the type of emulsion formed between oil and water will depend upon the size of the metal atom and upon its valence, since an atom with a valence greater than one will have more hydrocarbon chains attached to it.

As shown by experiment, sodium and potassium soaps form oil-in-water emulsions, and soaps of magnesium, calcium and other polyvalent metals form water-in-oil emulsions. Harkins attributes the different emulsifying powers of these soaps to the shapes of their molecules, the shape depending on the valence of the metal. In all cases the hydrocarbon radical of a soap acting as an emulsifier is thought to be oriented toward

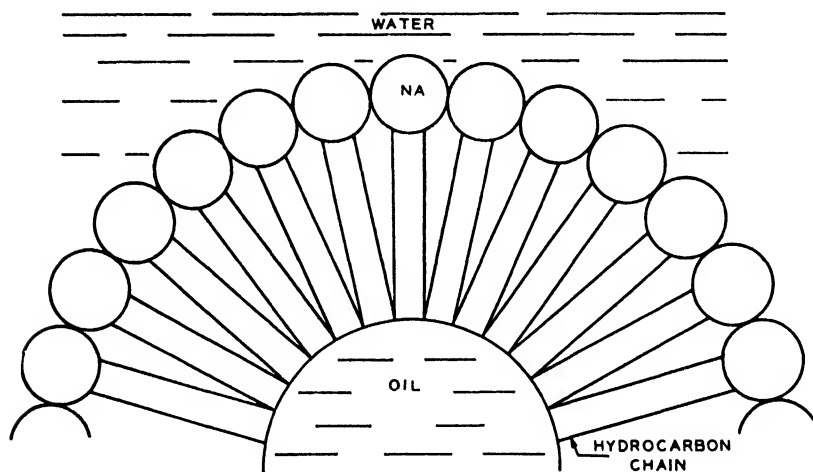


FIG. 13. A Drop of Oil Held Emulsified in Water by an Alkali Soap According to the "Oriented Wedge" Theory.

the oil, the salt group toward the water. The shape of the molecules, however, is radically different if each metal atom holds one fatty acid group instead of two or more. Quoting Harkins⁹⁹: "The molecules act as oriented, truncated cones, but in two dimensions as wedges, so this may be called the 'oriented wedge' or 'truncated cone' theory of emulsion. The conical shape of the molecule is conditioned by the relative areas of the cross-sections of the head, or polar part, of the molecule, and of the hydrocarbon chains at the other end." On the basis of this theory, when one oleate group is present in the molecule, the end holding the metal atom will tend to be the larger. At the interface the oriented film will, therefore, be concave toward the oil side and an oil-in-water emulsion will result. When the soap molecule contains two or three oleate radicals, as in the

case of soaps of the alkaline earths and heavier metals, the nonpolar (hydrocarbon residue) end of the molecule will tend to be the larger. The film with the oriented molecules will be concave on the water side, giving rise to a water-in-oil emulsion. Such an orientation in emulsions of both types is presented in Figs. 13 and 14.

In Fig. 13, the NaOOC end dips into the water, while the hydrocarbon end is submerged in the oil. The film is convex on the water side.

Zinc soap in Fig. 14 makes the interface convex toward the oil side; aluminum soap gives a still greater curvature and more stable emulsions of water in oil.

The particle size of the emulsion has been related¹⁰⁶ to the dimensions of the adsorbed emulsifier molecules. As an illustration, the case of an oil-in-water emulsion with the polar group of the emulsifying soap larger than the other end of the molecule and directed outward has been considered. The size of this polar group as compared with the remainder of the molecule will then determine the shape of the "truncated cone." The larger the polar group, the greater will be the concavity of the oriented layer on the oil side and the smaller the droplet.

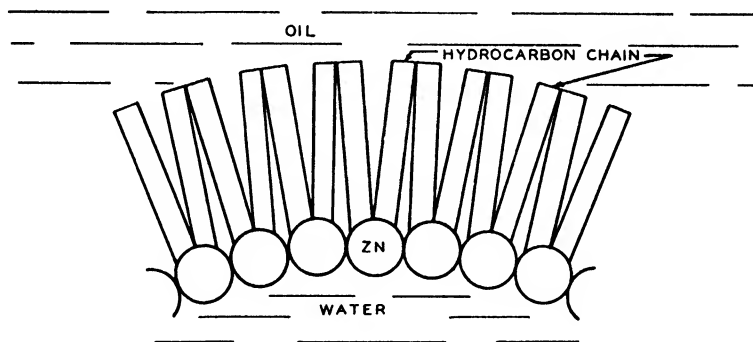


FIG. 14. A Drop of Water Held Emulsified in Oil by a Heavy-metal Soap According to the "Oriented Wedge" Theory.

Langmuir¹⁴⁴ states: "The size of the colloidal particles is determined by the difference in size between the two ends of the molecules, just as the size of an arch is dependent upon the relative size of the two ends of the stones of which the arch is constructed." To show that orientation determines the size of emulsion particles, Harkins and Keith¹⁰⁸ prepared a series of emulsions in which the emulsifying agents were lithium, sodium, potassium and rubidium oleates. The metal atoms in these soaps increase in size in the order in which the metals are listed. According to the orientation theory, this indicates that the sodium oleate film should be more concave toward the oil than the lithium film, and the particles in the emulsion stabilized by sodium oleate, therefore, should be of smaller average diameter than the particles in the lithium oleate emulsion. Similarly, the potassium atom being larger than sodium, potassium oleate

should give rise to smaller particles than sodium oleate, and rubidium oleate to smaller particles than potassium oleate. This reasoning has apparently been confirmed by their experiments, as these investigators found a regular decrease in the average size of the emulsion particles, going from those made with lithium oleate to those stabilized with rubidium oleate.

Finkle, Draper and Hildebrand⁷⁰ undertook a systematic study of the applicability of the orientation theory, first proving why the external phase is a more appropriate solvent for the emulsifier. The soaps of the alkali metals are more soluble in water, the others more soluble in the nonpolar liquid. The soaps of iron and aluminum have more symmetrical and fewer polar molecules and would, therefore, be expected to dissolve readily in solvents of low polarity, whereas the alkali-metal soaps, consisting of a single chain with a high polar end, do not dissolve readily in nonpolar liquids, but can form clusters with the hydrocarbon chains dissolving "colloidally" in water. These investigators considered the question whether different degrees in the curvature of films of different soaps should yield droplets of different sizes, and also the distribution of a large number of drops among different sized intervals. From the data obtained, cesium soap gives the smallest and sodium soap the largest drops; therefore, the curvature of the films actually differs in the direction predicted by the orientation theory of Harkins, according to which the order is in accordance with the valence and the atomic diameters of the metals; particles with only a few polar groups would remain largely in the oil phase, and vice versa. This explains Bancroft's rule that an emulsifier causes the phase in which it is dispersed to become the external phase of the emulsion. Later investigation tends to confirm the theory that orientation does take place at emulsion interfaces, but emphatically contradicts the idea that droplet size and emulsion stability are controlled by the size and shape of the molecules of the emulsifier, *i.e.*, the oriented wedge theory fails.

Harkins and Beeman¹⁰⁵ applied the orientation theory to a series of oil-in-water emulsions made with sodium, potassium and cesium oleates, as well as to water-in-oil emulsions stabilized by the oleates of aluminum and magnesium. The size distribution curves obtained for the dispersed particles were the same in all cases. Moreover, they were able to prepare a water-in-oil emulsion with a water-soluble soap and reverse it by mere dilution. These results do not indicate a dominating influence exerted by the shape of truncated cone molecules.

Harkins' idea that phase relations (direction of curvature of interface) and size of particles (magnitude of curvature of interface) in emulsion systems are determined by the orientation of wedge-shaped molecules of the emulsifier in the interface between the disperse phase and the dispersion medium was confirmed by some investigators, while others found it inconsistent. Two claims have been made in favor of the theory as stated by Stamm and Kraemer²⁵⁶ in their criticism of the orientation theory: (1) that it explains the decrease in the prevailing size of particles

with a change in emulsifying agent from sodium to potassium or cesium soaps, and (2) that it explains the change in phase relation upon changing the emulsifying agent from an alkali soap to an alkaline earth or an iron or aluminum soap. Neither the original evidence for the theory nor the consequences predicted by the oriented wedge theory have been completely confirmed.

According to Stamm and Kraemer, from the investigations of Finkle, Draper and Hildebrand^{70,71} and of Harkins and Keith,¹⁰⁷ it follows that the number distribution curves do not provide an appropriate basis for correlating the size of particles in an emulsion with the supposed wedge arrangement of the molecules of the emulsifier. Rather, they are of the opinion that the wedge theory requires a comparison of surface distribution curves of emulsions with different stabilizing agents. A decrease in the radius of curvature would be expected to occur at the interface with an increase in the wedge arrangement of the emulsifying molecules, and this corresponds to the maximum of the surface distribution curve defining the most probable radius of curvature at the interface of the emulsion. The maximum of the surface distribution curve corresponds to a greater particle radius than the maximum of the number distribution curve. Harkins⁹⁹ states that the most probable radius of curvature in an emulsion stabilized by sodium oleate is more than 750 times the apparent length of the oleate molecules. It seems unlikely therefore that, because of the presumed wedge shape, the oleate molecules determine the radius of curvature of such relatively large drops to any apparent degree. The volume and surface distribution curves, determined by sedimentation and microscopic methods by Stamm and Kraemer, failed to reveal any significant variation in the positions of the maxima for emulsions with palmitates of sodium, potassium, or cesium as stabilizers. The same conclusion was reached by Finkle, Draper and Hildebrand, and also by Harkins and Keith. The total interfacial area in the emulsion has been found to be constant for sodium, potassium and cesium palmitates within the limits of experimental error. Stamm states it is also hazardous to suggest that aluminum or iron soaps function as emulsifying agents in the form of single molecules oriented at the interface.

Briggs and Schmidt³³ claim that flocculent masses of what is perhaps aluminum hydroxide exist in emulsions stabilized by the use of an aluminum soap. Stamm and Kraemer further report an inconsistency between the facts and the wedge theory, where the relative influence of potassium palmitate and potassium chaulmoograte upon the stability of emulsions is concerned, judging from the results of Harkins and Beeman.¹⁰⁴ Likewise, according to Seifriz,²³⁵ the wedge theory is apparently not sufficient reason to anticipate reversals of phase relations in a series of aqueous emulsions of various petroleum distillate fractions stabilized by casein. The oriented molecule hypothesis assumes that the large or polar end of the molecular wedge, in the case of an oil-in-water emulsion stabilized with casein, would be the casein end of the associated molecule of casein and the hydrocarbon; and the membrane would, therefore, bend

with the oil ends of the interfacial molecules toward the inside. In the water-in-oil type of emulsion, the polar ends of the associated interfacial molecules become the outer surface of the stabilization membrane. Seifriz also obtained a regular shifting of the phase relationship by emulsifying a series of oils of increasing specific gravity with the same emulsifying agent. Seifriz, discussing his results in the light of the oriented wedge theory, does not find the two incompatible. The most serious hindrance is the assumption that there is an increase in the diameter of the hydrocarbon molecule with an increase in the specific gravity of the oil. The hydrocarbon chain is regarded ordinarily as increasing in length only when more carbon atoms are added, increasing the weight. However, it is believed that the hydrocarbon molecule increases in diameter as well as in length with increase in specific gravity. Stamm and Kraemer state that Sanyal and Joshi, as well as other investigators, believed the reversal of phase relations to be brought about by a change in the volume composition of an emulsion, even in the presence of sodium oleate. This fact has not heretofore been reconciled with the oriented wedge theory.

It appears that considerable experimental evidence is contrary to the oriented wedge theory. Perhaps the shapes and sizes of the molecules of the emulsifier have been overemphasized, judging from observations on the influence of volume composition and methods of emulsification and homogenization upon phase relation and degree of dispersion. Stamm states that it is difficult to see how the shapes and sizes of molecules in the interface could directly and mechanically or geometrically determine the size of the drops formed. Seifriz²³⁵ points out that considerable difficulty is found in accepting the oriented molecular wedge hypothesis as an explanation for the type or stability of an emulsion. The hypothesis presupposes a monomolecular film, or at least a membrane of molecular dimensions, whereas the membranes surrounding the dispersed globules of many of the emulsions considered in the literature are sometimes visible to the naked eye and often, when stiffening sets in, separate as permanent structures. This statement is not in accordance with the views on adsorption.

In measuring the surface tension of many benzene derivatives, Sugden^{261, 262, 263} believed that on the basis of the data obtained, the Langmuir-Harkins hypothesis of the orientation of molecules on a liquid surface leads to the prediction of regularities in the total surface energy of benzene derivatives. Thus, even if the surface molecules of a liquid do possess a definite orientation, the total surface energy is not determined simply by those groups which are directed outward, but by the molecule as a whole. Sugden states that, according to Langmuir, Harkins, Davies and Clark, the total surface energy of a pure liquid is determined largely by the orientation of the molecules in the surface layer. This view involves two hypotheses: (1) that the molecules in the surface layer of a liquid are so oriented that the more strongly attracted groups are closer to the mass of the liquid than those parts of the molecule which have less residual affinity; and (2) that the total surface energy of the liquid is

determined chiefly by the external groups of atoms and is only slightly affected by the strongly attracted groups which are drawn into the body of the liquid. Further, he develops theoretical arguments from which it can be seen that no evidence is obtained for or against the existence of a layer or of oriented molecules by a comparison of the total surface energies of related substances. However, since such oriented layers do seem to exist to some extent in certain solutions, as well as in thin films of insoluble substances on a water surface, it is interesting to inquire what limitations the kinetic theory sets upon orientation taking place to any extent in a pure liquid. An oriented layer contains molecules which have lost their degree of freedom, namely, rotation, translation, and vibration, according to the theory of the equi-partition of energy. This means a loss of $3 \times 1/2RT/N$ ergs per mol of kinetic energy which should reappear as potential energy at the surface. From the density of benzene at 25°, it follows that the average cross-sectional area of the benzene molecule (assumed to be symmetrical) is 28×10^{-16} sq cm. Hence, the potential energy of one sq cm due to the forces producing a monomolecular oriented layer is $\frac{3}{2} RT/N \times 28 \times 10^{-16}$. Taking $R = 8,315 \times 10^{-7}$, $T = 298$ and $N = 6.06 \times 10^{23}$, this becomes 21.9 ergs/sq cm. Since the free energy of benzene at 25° is about 25 ergs/sq cm, it is evident that the forces found by experiment to exist in the surface layer are of the right order of magnitude and are capable of bringing about some degree of orientation.

Einstein⁸¹⁻⁸⁴ considers that the replacement of surface molecules by diffusion from the liquid mass is difficult to calculate. His theory leads to the conclusion that within the liquid the time required for a molecule to move through its own diameter is of the same order of magnitude as that required for rotation through 180°, or 10^{-9} second. From our present knowledge, according to Sugden, it is impossible to prove that orientation occurs at the surface of a pure liquid. It has been shown, however, that such an ordered arrangement of the surface molecules, if present, does not affect the total surface energy, as would be expected, and that the kinetic theory sets definite limits on orientation if present to any great extent. From this consideration, the surface properties of pure liquids are best accounted for by a theory of random distribution of surface molecules.

The mechanism of emulsification by soaps has been explained by a modification of the wedge theory.¹⁵⁹ The original form of the wedge theory would be destroyed if it could be shown that the molecules in the interfacial film are by no means closely packed. Griffin⁸⁸ actually showed that the area occupied by a soap molecule at the oil/water interface was 44 \AA^2 , whereas Harkins and Beeman¹⁰⁴ showed that an emulsion could be formed with a larger interfacial area.

Lyons'¹⁵⁹ film experiments proved that a residual bimolecular film of acid soap was the stable configuration in alkaline solutions. He assumed that a "bimolecular leaflet" might be present at the oil/water

interface, in which case it would have a profound influence on the emulsifying power of the soap solution. The existence of the bimolecular leaflet at the surface of soap solutions seems to be well established, and the similarity between frothing ability and emulsification apparently confirms the presence of this bimolecular leaflet at the benzene/water interface. In solutions where a benzene-in-water emulsion is more stable, film experiments show that the lower layer of the bimolecular leaflet was not completely close-packed. In very alkaline solutions, where a water-in-benzene emulsion is more stable, the bimolecular film has considerably less than half the area of the original monomolecular film. In solutions where the two layers are equally packed, the emulsions are of almost the same stability. These observations, according to Lyons, support the view that emulsification depends on the presence of a bimolecular leaflet, and that a monomolecular film shows little tendency to form emulsions.

A film exists whenever a layer which has a composition differing from that of the body of the liquid or solid is present at the boundary surface, provided the area and form of this layer are independent of gravitational forces. Film formation versus lens formation is determined by the balance of interfacial forces. Whenever the area and the form of the layer depend upon both the surface and gravitation, a lens results. The question is raised whether Lyons considered this fact in his theory of a "bimolecular leaflet" in the interface.

Lyons presents the mechanism of emulsification as follows: When a soap molecule is first adsorbed at the interface, it gives a double film packed the same on both sides. In less alkaline solutions, the lower layer will be less densely packed than the upper layer, and equilibrium is reached either by a transference of molecules across the interface or by curvature of the boundary. In emulsion formation, the latter effect predominates. To increase the curvature of the lower layer of the initial symmetrical film, the boundary is curved with the upper layer toward the inside, giving an oil-in-water emulsion. A similar analysis accounts for the stability of water-in-oil emulsions in very alkaline solutions where the lower layer is probably more closely packed than the upper. Over the range within which a symmetrical leaflet is stable, the boundary will not be likely to curve in either direction, and neither form of emulsion will be more stable than the other.

Cassel^{43,44} derived a criterion for the stability of emulsions based on thermodynamic principles and known adsorption isotherms. He showed, in agreement with Bancroft's rule and Ostwald's solid substances rule, that an emulsion system remains stable by small additions of a stabilizer, exceeding a minimum concentration, whereas with larger additions (except in the case of monomolecular adsorption) it again becomes unstable. The empirical course of adsorption isotherms is determinative for the stability range of films. The thermodynamic theory of adsorption on curved surfaces leads to a relationship corresponding to that found by Gibbs-Thomson for the dependence of vapor pressure on droplet size. In this connection, the basic idea has been deduced^{44a} that emulsions may

be stable if the density of the emulsifying boundary films is greater for surfaces with a greater curvature than for those with a smaller curvature. According to Gibbs-Thomson calculations, a system made up of small, globule-like drops is unstable because its vapor pressure is increased by surface curvature. When an emulsifier (stabilizer) is used, the stability of the emulsion depends on the stability and impermeability of the formed film. If this film stands in equilibrium with the limiting phases, the thermodynamic potentials of the emulsifier are the same in the whole system. This value is given by the capillary pressure, which acts upon the internal phase, and may be expressed by the equation:

$$\mu_r = \mu_0 + 2\sigma/r(D_{in} - D_{ex})$$

where μ_r and μ_0 are the potentials of the curved as well as of the flat films; σ , the interfacial tension; r , the radius of the particle, and D_{in} and D_{ex} , the densities of the emulsifying substance in the internal, as well as the external phase. If the film is stable, $\mu_r < \mu_0$ and $D_{ex} > D_{in}$. Cassel's thermodynamic theory accounts for the fact that diminution in the radius increases the stability of emulsions and also expresses Bancroft's rule governing the reversal of emulsion type. Conditions of stability for emulsions containing a stabilizing agent have been discussed recently by Boutaric.²⁸

Schulman and Cockbain's recent investigation^{234c} seems to indicate that a stereochemical packing at the oil/water interface is essential to the formation of a stable emulsion so that a condensed liquid film will form. This interfacial film is electrically charged. The stability of these films is dependent on van der Waals' forces of attraction between the nonpolar parts of the two components (oil- and water-soluble) and on the interaction between the respective polar heads. Alteration in the size of the nonpolar residues and the nature of the polar heads cause alterations in the molecular packing and stability in the interfacial complex films, and therefore in the stability of the investigated Nujol-in-water emulsions.

In Fig. 15 Schulman and Cockbain present diagrammatically three different complexes showing marked differences in the stabilizing power. Emulsion stability is a function of stereochemical packing at the interface, closely packed condensed complexes giving an excellent emulsion.

The theory of orientation, in spite of its variations, or the consequences found or assumed by different investigators, is of great interest and significance, although more experimental work is required to prove its application to emulsion systems. However, there seems to be evidence that the molecules of the emulsifier are actually oriented at the interface between the two phases of an emulsion; but whether the particle size, amount of curvature of the interface, or stability is determined by the geometric configuration of the molecules has yet to be proved experimentally.

Summary

Progress in our knowledge of emulsion systems indicates certain necessities in the manner in which future investigations in this field should be

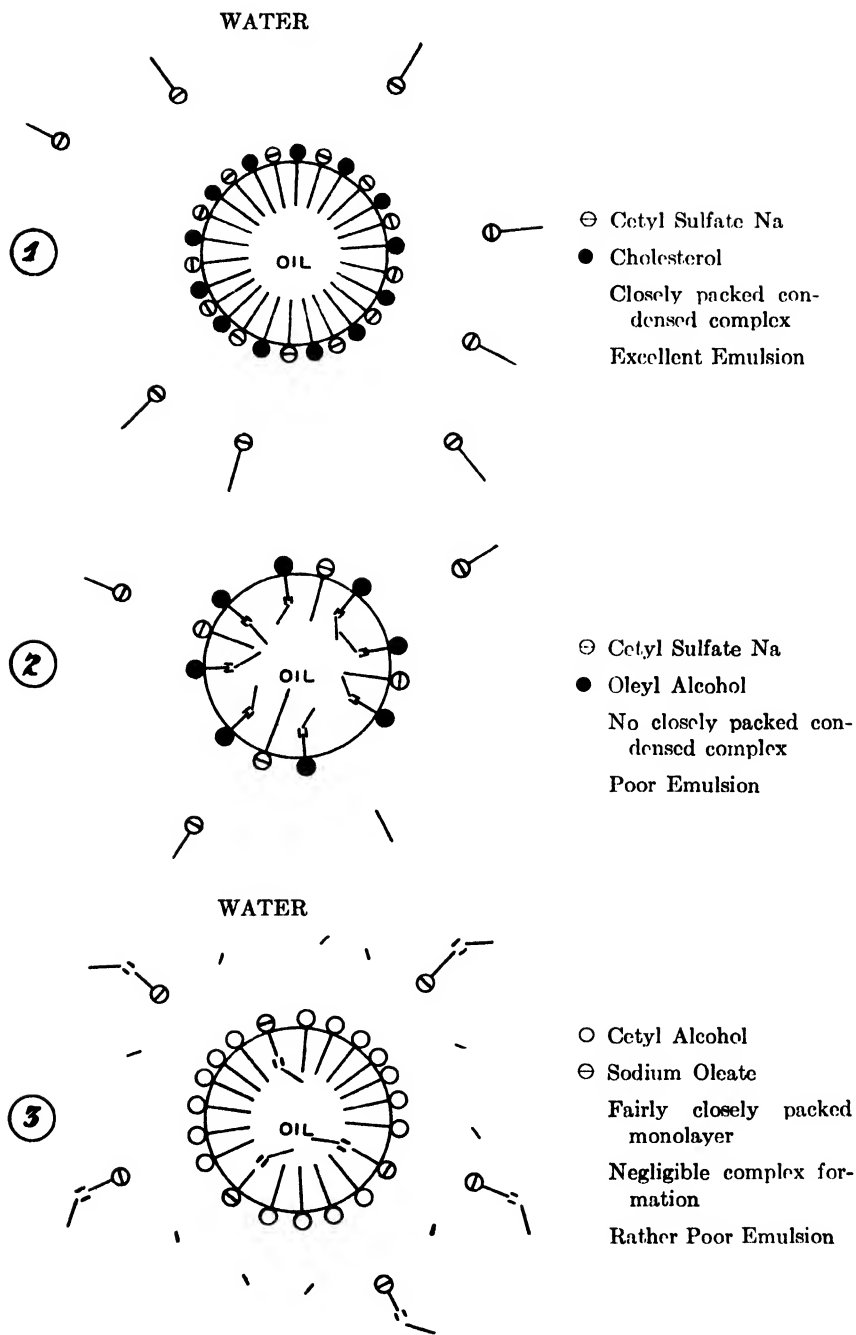


FIG. 15.

carried out: (1) a logical and separate grouping of factors influencing emulsification, permanence of the system formed, and its transition from one type to another; (2) more accurate methods of investigation; and (3) only emulsion systems similar in nature and type should be compared with respect to their various properties, and then only under comparable conditions.

1. Factors Influencing Emulsification

Surface tension, as well as interfacial tension, acting as a contractile force, draws one of the components of an emulsion system into a series of spherical droplets and separates an intimate mixture of two immiscible liquids into two single phases separated by the smallest possible interface. The efficiency of a third substance—the emulsifier, added to the system to promote emulsification—is often indicated by its ability to reduce the interfacial tension between the two original liquid components of the system. A low interfacial tension between oil and emulsifying agent is the result of adsorption of the latter in the boundary of oil and water, where it is spread out into a thin film. Low surface or interfacial tension decidedly assist emulsification.

Viscosity plays a rather subordinate part in emulsion formation. From the standpoint of emulsification, two kinds of viscosities should be considered, namely, that of a molecular dispersoid having true internal friction and resisting molecular motion, and that of an emulsion which offers no hindrance. Some effect upon emulsification may be expected from colloidal liquid emulsifiers, such as albumin, starch, and glue. In case of Pickering's solid emulsifiers, the efficiency is not less than that of molecular and colloidal solutions. In both cases, emulsification may be interpreted by influence of viscosity. High viscosity in the external phase inhibits stabilization of the interface by retarding diffusion of the emulsifying agent into it, thereby hindering emulsification. Viscosity is not a primary factor in, or cause of, emulsification, although it may increase emulsion stability; in some cases it is important only because of the hindrance offered to the coalescence of dispersed globules.

Solubility of the emulsifying agent may be related to its emulsifying power with respect to whether it is molecularly or colloiddally soluble, and whether the phase in which it is soluble is external or internal. One definition of a good emulsifier is that it be soluble and present in the external phase. As to whether the emulsifier is always in a colloidal state at the time it produces emulsification, equally valid and generally accepted evidence indicates that a good emulsifier may be molecularly or colloiddally dispersed, or may exist as macroscopic particles. However, classification of emulsifiers with respect to their emulsification ability based on their solubility is of great importance.

The ability of colloidal emulsifiers to combine with water to form a hydrate in the process of emulsification has been overestimated. The different emulsifying efficiencies, ascribed to varying hydration, of substances acting as good emulsifiers may be significant in some cases; but

the postulate that oil is well emulsified by a hydrophilic colloid when just a sufficient amount of water is present to form a hydrate is incorrect.

The degree of dispersion of a liquid or of a solid substance used as an emulsifier is of importance in producing emulsification. The greater the dispersion of the emulsifier, the larger the active surface producing the emulsion. On the other hand, the concentration of the emulsifier determines whether there is sufficient emulsifying agent present to induce emulsification, but it is incorrect to assume that emulsification depends solely on particle size. In no way is it correct to state that the average size of globules in an emulsion depends on the size of particles of the emulsifier used. Whether the size of particles of the emulsifier in itself accounts for emulsification, or the chemical behavior of the emulsifier or the gravitational or other forces acting simultaneously in the system are responsible for the formation of an emulsion, is hard to say. It is believed that the properties of the particular emulsifying agent in a particular oil/water system are of decisive importance in emulsification phenomena. The viewpoint that emulsification depends solely on the minuteness of division of the emulsifier is not justified in the case of solid emulsifiers.

In the case of oil-in-water emulsions, in order that solid particles of emulsifiers be emulsified, they must not have a tendency to agglomerate, but must be adsorbed at the oil/water interface, that is, must be more readily wetted by water than by oil; the opposite is true of water-in-oil emulsions. When liquid molecules and those of the solid surface attract one another, wetting takes place, as a result of which the liquid spreads to an extent determined by the spreading coefficient, given by the contact angle which the surface of the liquid makes with the liquid/solid interface. The size of the contact angle is determined by the balance between three interfacial tensions: liquid A/liquid B, liquid A/solid, and liquid B/solid. The liquid/liquid interface is inclined in the direction of the liquid possessing smaller spreading ability.

In investigating the factors governing emulsification, the following measurements should be carried out for an emulsion system: (1) interfacial tension; (2) viscosity of the oil component (viscosity of the emulsion system, both initially formed and after emulsification); and (3) solubility of the emulsifier with regard to its degree of dispersion (colloidal or molecular) and the phase (external or internal) in which the emulsifier is present. For a solid emulsifier, the degree of dispersion, action of gravitational force (sedimentation), and chemical behavior should be tested. The wettability of both components of the emulsion must be measured separately, as well as the angle of contact of the interface with the solid, and the adsorption ability at the interface, considering also the curvature of the boundary. In the case of liquid emulsifiers, the spreading ability of one liquid upon the other should be determined.

During emulsification measurements, the physical conditions to be considered are: temperature, time of emulsification, type of mechanical treatment, and homogenization of the emulsion formed.

2. Factors Influencing Stability of Emulsion Systems

The permanent state of emulsion systems is likewise governed by its specific factors, principally by the action of two opposing forces: (1) the surface tension tends to bring about coalescence of the dispersed globules, and (2) the cohesive force of the film of the emulsifying agent resists coalescence. The stability of emulsions increases when the interfacial tension decreases. To some extent, and in certain cases, viscosity among other factors improves the stability of emulsion systems. A high superficial viscosity may account for the resistance offered to the withdrawal of films from between the oil droplets, and consequently for the permanence of the emulsion. Likewise, in instances in which interfacial tension is not strong enough to withdraw the interfacial film fast enough, and where the emulsifying agent has a greater internal viscosity, the thinning of the protective film occurs so slowly that the emulsion is maintained in a permanent state.

Even if an equilibrium in an emulsion system corresponding to the permanent state is established, physical factors, such as temperature changes, ageing, and hydrolysis, may readily displace it. In this sense, knowledge of the nature of the emulsifying agent, as well as that of the stabilizer, is of great importance. Physical factors affect the molecular or colloidal emulsifier differently, and this fact is reflected in the maintenance or destruction of the permanent state. The rate of separation or disintegration into layers obviously is a function of the difference in density of the phases, the viscosity of the continuous phase, the velocity of diffusion, and the degree of dispersion. The size of the globules constituting the disperse phase of an emulsion is an important factor in determining its permanent state; a stable emulsion usually contains all sizes of globules with a maximum of 1.0 to 1.5 microns, the percentage of larger globules being small. While little is known about the relationship between the physical properties and the average size of globules in the disperse phase, it is an established fact that the degree of stability of an emulsion may be measured by the change in number distribution curves with time, *i.e.*, during the ageing of the system, and that an emulsion approaching the unstable state is characterized by the appearance of large globules as the result of coalescence and aggregation of smaller globules.

Since the stable state corresponds to a strictly spherical shape, the appearance of irregularities in the shape by microscopic examination is a proof of a broken emulsion. The reason why globules resist coalescence into larger aggregates as well as for the destruction of the static equilibrium, lies in the existence of electric charges on the globules. Those of the disperse phase are electrically charged in such a manner that a charged double-layer constitutes a kind of a spherical condenser, its thickness being small in comparison with the radius. Globules with a charge of the same sign repel one another on approach, preventing coalescence. Naturally, the finer the division the less chance there is for coalescence to take place, and the more stable the emulsion. Of course,

the presence of electrolytes and their action, mobility of Brownian movement, and volume concentration are factors influencing stability in their turn. Action of electrolytes on oil-in-water systems often causes a discharging effect on globules, as well as discontinuance of Brownian movement. Brownian movement depends on thermal agitation of molecules, on the mass, on the difference in the specific gravity between the disperse and the continuous phase, on viscosity, and on pH value. If there is no material difference in specific gravity between the phases then, after discharge by electrolytes, only a change in the degree of dispersion takes place, but not precipitation.

Complete coagulation of an emulsion system involves not only the action of electrical forces, but also that of capillary forces. It is postulated that normal coalescence is prevented by the electric double-layer, which must first be broken. The potential difference between the dispersed globules and the dispersion medium and the electric charge carried by dispersed globules is directly related to the stability of emulsion systems. At the oil/water boundary there is a contact potential. When this decreases, the stability likewise decreases; because of a decrease in the strength of the electric double-layer, the latter can be readily destroyed and thus bring about coalescence of the globules. With respect to the potential difference across the double-layer in the case of oil-in-water emulsions, it is postulated that if it exceeds a critical point of 0.03 volt the emulsion is stable, but below this point coagulation should take place.²⁷³ As with other suspensions, in addition to the effective charge and the electrokinetic behavior of dispersed particles, the stabilization effect of certain ions must be considered for some emulsions. The presence of flocculating ions of various electrolytes in the system may reduce the concentration of those ions acting as stabilizers.

The protection of an emulsion against breaking is assumed to be caused by a film at the interface. The nature of this film, its thickness and change with time, are factors closely related to the concept of emulsion stability. Not only does a special thickness of the film at the interface (often specified as monomolecular) contribute to the stability of an emulsion, but also to the manner in which molecules making up the emulsion are oriented in the interface. The molecules of the soap and the emulsifier tend to orient themselves so that the boundary molecules are in a position to permit the transition from one liquid phase to the other to occur with the least possible abruptness. This orientation is also in accord with the general principle that at the surface an arrangement which gives the lowest free energy will be the most stable. The molecules which make the transition from the interior mass to the dispersion medium, or the molecules of the film, are supposed to fit the curvature of the drop and by a definite size produce a stable system. Thus the stabilizing ability of an emulsifier is supposed to be indicated by the curvature of the film in the interface, whether it is more or less concave toward the oil phase, and by the size of the average droplets fitting the curvature.

Experimentally, the state of stability of an emulsion may be measured by: (1) size frequency analysis; (2) electric charge (cataphoresis) and potential difference across the double-layer between the disperse phase and the dispersion medium; (3) thickness of the protective film at the interface, measured in time intervals (excluding the action of hydrolysis); (4) surface, as well as interfacial tensions as functions of time; and (5) viscosity and specific gravity.

3. Factors Producing Inversion of Phases in Emulsion Systems

As a rule, emulsion types cannot be reversed by merely changing the volume ratio. Usually a certain emulsifying agent will form an emulsion of one type only, regardless of the phase ratio, but there is always a maximum amount of oil which may be emulsified. It is assumed that at a critical ratio of water to oil so much of the emulsifier soap would be present that it could surround the oil drops without formation of intermediate spaces of more than molecular dimensions. When not enough soap is present to surround the droplets completely, the surface possesses a higher surface tension and the system becomes unstable. For an oil/water type of emulsion, a liquid emulsifier is likely to be soluble in the external phase, whereas a solid emulsifier is likely to be wetted more by water than by oil. For the reverse emulsion type, water-in-oil, the opposite conditions for the emulsifier are implied. The inversion point of emulsion systems is influenced by changes in various physical conditions under which the system exists: (1) a rise in temperature favors the oil-in-water type, whereas lowering of the temperature is more advantageous for the reverse type; (2) electrolytes or alkali soaps stabilize only the oil-in-water emulsions, but polyvalent soaps stabilize only the water-in-oil emulsions; and (3) dilution with water effects a change in the type of emulsion due, partially at least, to a transfer of the soap to the aqueous phase or to the displacement of the equilibrium between emulsifying tendencies of opposed emulsion systems, so that stabilization of the oil-in-water type in the end is in the ascendancy. However, in the latter case, a dual emulsion, rather than one of the inverted type is formed. The greater the dilution or the greater the distance between the oil globules in an emulsion, the larger the proportion of multivalent electrolytes required to bring about reversal of phases. Mechanical treatment, such as vigorous restirring of the emulsion, is one of the variables which, under certain conditions of the system, may cause inversion of the emulsion.

Free fatty acids and alkalies shift the inversion point in opposite directions. The differences in the percentage of electrolyte required to produce reversal of phases indicate their varying protective action. The nature of the emulsifier, as far as phase inversion is concerned, is involved because hydrophilic colloids tend to make water the external phase, whereas hydrophobic colloids tend to make it the internal phase. The hydration ability of the emulsifier may be important at times. Whether oil dispersed in water or water dispersed in oil results from emulsification

depends also upon orientation and the packing effect of the molecules of the emulsifier at the interface.

The size of the metal atom, as well as its valence, may also be related to the effect of reversing the type of emulsion.

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FOAMS

Introduction

A parallel exists between the concept of emulsions and that of foams. Not only are foams similar to emulsions, but they may be considered, to a certain extent, as concentrated emulsions having a gas instead of a liquid as the dispersed component. On the other hand, the fact that the formation of an emulsion is often accompanied by the formation of foam indicates that, at least in these cases, foam systems originate under the same conditions as emulsion systems. Oils which are readily emulsified in water act as foam-forming substances, but difficultly emulsifiable oils, such as cedar or castor oil, show very little tendency to form foam. Foams, as well as emulsions, are generally three-component systems, that is, they require the presence of an agent for their formation. Factors influencing the origin of foam systems and those influencing their ability to sustain themselves indicate another similarity between the properties of emulsion and foam systems.

Three stages may be differentiated in the life of dispersion systems such as emulsions and foams: (1) origin; (2) maintenance of the stability of the system formed; and (3) transition to the unstable state. Factors and forces governing different stages in the existence of a foam comprise the physical chemistry of the system in question.

Foam Formation

Origin and Mechanism

The formation of a single lamina. Foam is a formation in which macroscopic, microscopic and/or ultramicroscopic gas bubbles are separated by micronic or submicronic liquid layers (skins). Therefore, foam is a union of laminae. The formation of a foam occurs in the same manner as the formation of a single liquid lamina. Each film formed serves as a basis for the formation of other surface films; consequently, knowledge concerned with the formation of a single film may account to some extent for a number of films, called in the aggregate "foam."

The construction of a foam system may be described as follows: A bubble of air rising in a liquid reaches the surface but does not break through; it rather lifts up a film in the form of a spherical wedge. A second bubble rises to the top, approaches the surface at a certain point, and is placed under the first film. This determines the formation of a second lamina which lifts the first film on one side, so that the amount of air enclosed by these two laminae respectively is separated by a portion of the second lamina, as well as by a partition of liquid. In the event the second lamina originates at a distance, the spherical wedge of the first is then completed; the capillary forces and flotation of light bodies assist the second bubble to approach the first in order to create

a tangential contact, provided they are not separated by too great a distance, which is not the case in foam formation.

Actually, only a part of a bubble reaches the surface and wets it. The faces of the bubble change in curvature before they touch tangentially, and the same change occurs also along the line on which a bubble is bound to other bubbles. Obviously, because of their liquid nature, the two laminae cannot meet each other either at their angles or at their linear edges; for continuity, it is necessary that they be formed along the line of meeting in a small area of concave surfaces placed perpendicular to this line. But this area is too small to be distinguished, as are the partitions, which unite to form a small mass, having its own curvature independent of the respective curvatures of the two laminae and dependent on the difference in the pressure exerted upon the sides of the two volumes of air enclosed. If these two volumes of air are equal, the two laminae belong to equal spheres, compressing the two volumes of air with the same intensity. But if the volumes of air are unequal, the two laminae belong to spheres of different diameters, exerting an unequal pressure on the two volumes of air. Consequently the partition, when subjected to equal pressure on both sides, is not curved, but plane; and when subjected to unequal pressure, it is distorted on one side, the partition diminishing until the pressure produced by it in the concave curvature counterbalances the elasticity of the air.

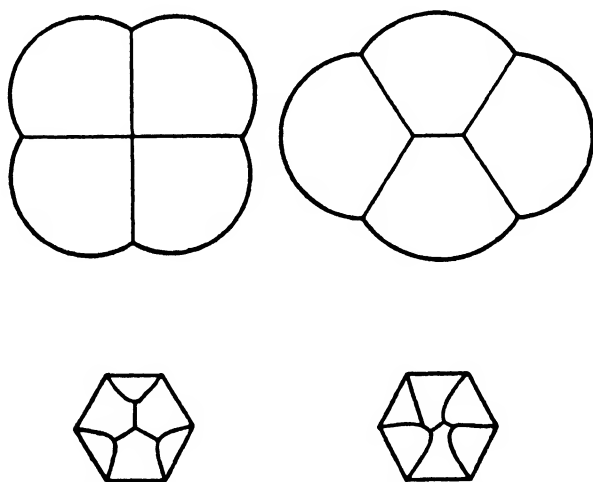


FIG. 1. A Group of Four Bubbles and a Projection of Assembled Curved Laminae.

Since air bubbles are always rising, the structure formed is lifted continuously. All laminae are layered with more or less symmetry, depending upon the difference in the volume of air bubbles and the distribution of points where they may reach the surface of the liquid, the air bubble structure growing higher and higher.

Observation reveals that this accumulation of bubbles is not governed by chance, but is subject to law; that is, innumerable bubbles join together in threes at equal angles in such a way that not more than four edges of three laminae pass through the same point, cutting laminae, as well as edges, at an angle of 120° . Therefore, foam bubbles, in cross-section, are hexagonal structures with equal angles of 120° .⁴⁴

In Fig. 1 a configuration of a group of four bubbles, assumed to be equal in diameter and combined rectangularly, is graphically presented. But since this structure is in a state of temporary equilibrium, a transition from it to a structure in which three laminae are joined together at an angle of 120° may occur. In this same figure there is also included a projection of assembled curved laminae connected with one another by other laminae extending the length of the prism.

In the formation of a foam, bubbles are formed in which more than three laminae come together, the laminae sliding over one another until conditions for true equilibrium are fulfilled. The motion of the liquid, when displaced by a bubble, lifts up the skin formed, and is such that it stretches the two surfaces where the liquid comes into contact with the air. The liquid film, or lamina, may be stretched only when surface tension and vapor pressure are small. In 1869, Mensbrugghe³⁷ proposed a formula for the equilibrium of a lamina resting on the same liquid from which it originated (Refer to Fig. 2 for graphic presentation).

In Fig. 2 the interior surface of a bubble is concave.

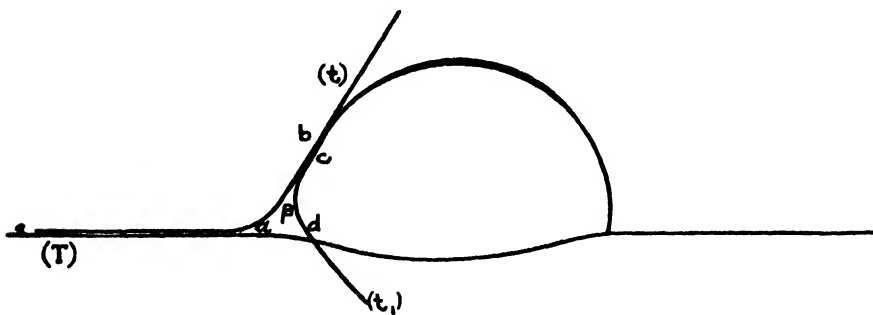


FIG. 2. Graphic Presentation of a Lamina Resting on the Liquid from which It Originated.

Forces acting in a lamina. The surface tension, T , of the external liquid at a , the horizontal components of two surface tensions t at b and c , and the horizontal component of a single surface tension t' at d are the forces which tend to displace the liquid contained in the area bounded by curves ab and cd and line ad (Fig. 2). (These tensions are all directed against the exterior of the small mass of the liquid.) If α and β represent angles formed by tangents with the horizontal in b or c and in d , then we have:

$$T = 2t \cos \alpha + t' \cos \beta$$

According to Mensbrugghe if, in the case of an aqueous soap lamina formed on the surface of the same liquid from which it originated, tensions T , t , and t' are equal, the equation is then written:

$$2\cos\alpha + \cos\beta = 1$$

Or, if the lamina is very large, the pressure produced upon the air enclosed is very low; therefore, β is close to zero, α close to 90° , and the lamina is hemispherical.

If the dimensions of the sphere decrease, the pressure of the air on the interior, as well as β , increases with a gradual decrease in α ; the lamina would then constitute a portion progressively smaller than a complete sphere. Also, it is evident that if $\cos\alpha$ is close to 1, then $\cos\beta$ is close to -1 . This is in the case of an extremely small air bubble; in the surface of the liquid, practically no bubbles originate.

Construction of a foam system. In passing from a single liquid lamina to a system made up of a number of laminae, it is of great importance to consider the surface tension factor. Quincke⁴⁶ and Marangoni³⁵ studied the conditions under which a liquid spreads into a thin film, concluding that: (1) Surface tension exists in all liquid surfaces and therefore in all films, and is independent of the curvature of the surface or film. This surface tension is the same for all directions of the surface or film and at every point. (2) Surface tension varies with the nature of the liquid. (3) For the same liquid, surface tension varies inversely with the temperature, but at ordinary temperature it undergoes little change.

Many hypotheses have been proposed to account for surface tension. According to Segner⁵⁶ it originates from the mutual attraction of molecules in the superficial layer tangential to the curvature of this layer; according to Mossotti,⁴¹ Hough,²⁰ and Dupré,¹² it depends upon the asymmetry of molecular action in the thickness of the superficial layer, although only minor differences in this type of asymmetry are involved; Hagen's¹⁷ hypothesis attributes surface tension to a great density of the superficial layer; the theories of Lamarle²⁹ and Henry²³ consider surface tension to be due to the contraction of the superficial layers, some of the molecules in this layer passing into the interior, thereby decreasing spreading.

According to the work of Laplace, who considered only the effect of curvature, the pressure from a concave layer in a state of equilibrium opposes a force originating in general hydrostatic actions. It must be borne in mind that convex and concave superficial layers exert a normal pressure on a liquid at each point, the superficial layer, meeting an opposing force, finally spreading after curving beyond a critical point. In other words, molecules in the same layer must be in a condition to spread tangentially. This is the reverse of Young's theory, which assumes surface tension, and shows that the tangential component of the surface tension around a given point has a normal pressure as a resultant, regardless of whether the surface is convex or concave. This pressure, as Laplace showed, exists only because of molecular attraction and may be analyzed

around a point into tangential components, each of which constitutes a surface tension.

Plateau states that surface tension is a result of curvature, but is independent of the value of this curvature. From an actual consideration of the two tangential components of a convex surface of a liquid and the initial pressure which causes their appearance, it is evident that, if the curvature decreases, this pressure decreases at the same time; but, on the other hand, the angle between the two components increases in such a manner that these components or surface tensions retain the same value as for the previous curvature. If the curvature decreases up to a point where it disappears, the component affected by pressure is eliminated and the two remaining components become prolongations of each other; therefore curvature is infinite, as in the case of plane liquid surfaces.

Another question to be considered is how surface tension penetrates similar surfaces, for instance, a film of liquid adhering by its edges to the surface of a liquid, or to other films. In the case of films, these partitions are invisible, but their existence is obvious. As previously stated, the faces of the bubbles change their curvature before they touch tangentially.

Conclusions

- (1) Foam is a union of laminae.
- (2) The mechanics of foam formation is similar to that of a single lamina.
- (3) The symmetry in the construction of a foam depends upon the difference in the volume of gas enclosed by a lamina.
- (4) The accumulation of bubbles in a foam follows Plateau's rule, that is, bubbles join in three at angles of 120° .
- (5) Physical factors involved in the spreading of a liquid into a thin film apply to foams, surface tension being one of them. Surface tension is the result of curvature and is independent of the value of curvature. It is the same at every point in all tangential directions. It varies with the nature of the liquid and inversely with temperature. The change in curvature of the faces of bubbles prior to their tangential contact is proof that surface tension penetrates a film.

Factors Influencing Foam Formation

Vapor pressure and surface tension. Not every gas bubble distribution in a liquid, as in a sol, can be called a foam. Foam formation combined with a great increase in surface is possible only when the surface tension of the foam components is small.

Pure liquids with low surface tension are close to their boiling points and have a high vapor pressure. Therefore, the thin liquid laminae of which foam is composed evaporate too quickly to form and sustain foam. On the other hand, when liquids have a low vapor pressure, their surface tension is too great. Low surface tension and vapor pressure, when present together in capillary-active substances, are favorable conditions

for the promotion of the foaming process.¹⁵ Capillary-active substances, when dissolved in a system, lower the surface tension and are adsorbed in the interface.

That a certain relation between foaming and surface tension of the liquid from which foam originates should be anticipated follows from the fact that solutions containing dissolved capillary-inactive substances not influencing surface tension do not produce foam. Foams do readily occur,

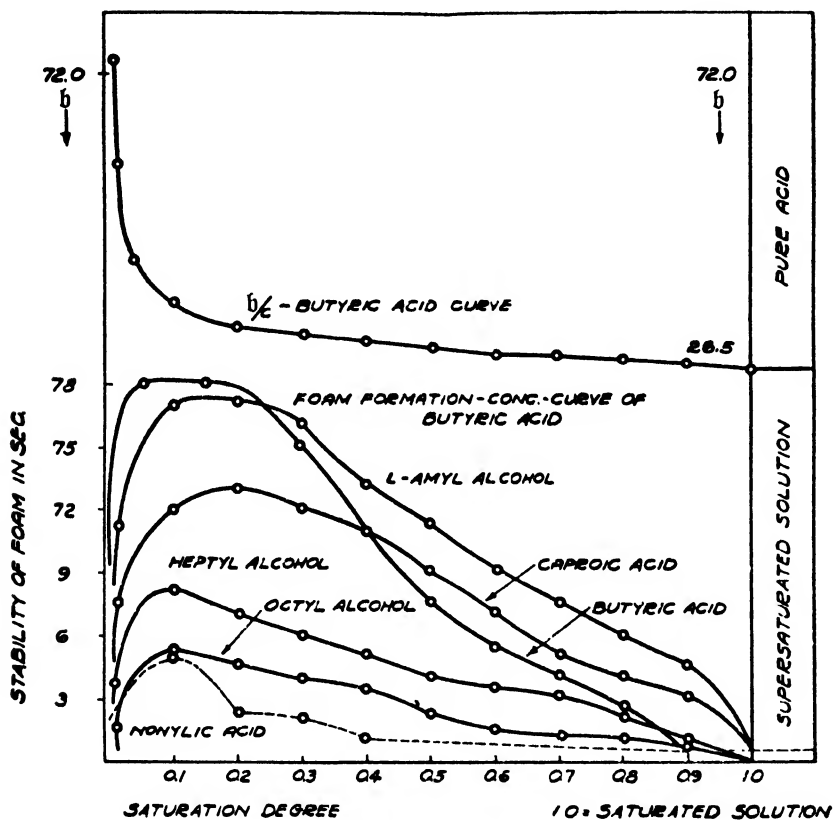


Fig. 3. Surface Tension and Foam Formation.

however, in solutions of surface-active substances, such as organic salts and acids, sugars, glycerins, alcohols, and esters. Of course, surface-active substances are foam agents only under definite conditions. In certain cases, discussed later, other factors, such as concentration, solubility, viscosity, etc., may overcome the influence of capillary activity. Bartsch³ proved experimentally (Fig. 3) that foam formation and lowering of surface tension are antagonistic when a certain concentration is exceeded.

Foam formation-concentration curves drawn by Bartsch for butyric, nonylic, and caproic acids and for octyl, heptyl, and amyl alcohols indicate

that these capillary-active, foam-forming substances lose their foaming ability when a certain saturation is exceeded. The upper curve σ/c of butyric acid has a shape indicating that the relationship between foaming ability and surface tension is lost in higher concentrations. The same experimenter also found that, even in the case of such strong capillary-active substances as sodium cholate or saponin, the foam-producing ability may be lost when supersaturation occurs. Wo. Ostwald and A. Steiner⁴³ proved with humus sols that a relation does not always exist between surface tension and foam-forming ability. Bartsch pointed out that oleic acid emulsions which do not foam show a pronounced foaming ability at certain concentration intervals, in which, as a rule, the surface tension is of an order of magnitude corresponding to that of water. By com-

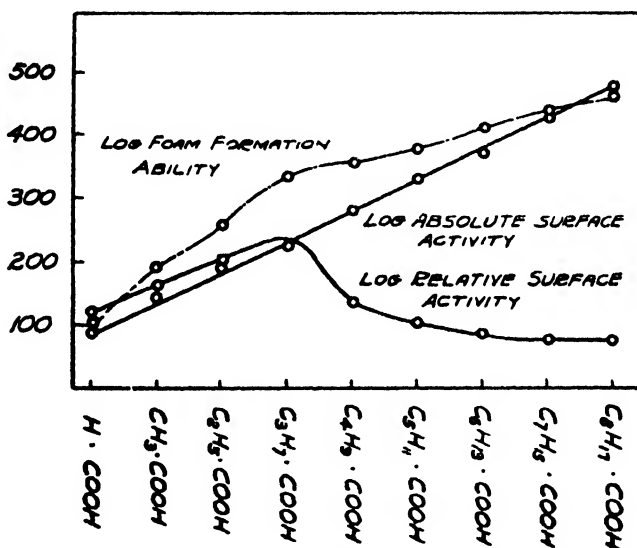


FIG. 4. Surface Activity and Foam Formation for More Dilute Solutions.

paring the foam-forming ability of various surface-active foam-forming substances, such as homologous alcohols and fatty acids, the relationship between surface activity and foam formation was found to be complex. A parallel was observed when concentrations were studied corresponding to the limited value for foam formation³ (Figs. 4 and 5, from reference 3).

When the maximum in foam formation was reached, the acids decreased the foaming ability in spite of an increase in surface activity, using members of the homologous series with limited solubility. The only regularity observed by Bartsch was in the group arrangement of surface tension values. The average corresponded to an optimum foam formation at 61 dynes for fatty acids and alcohols. In other cases, the decrease in foaming ability was parallel with the decrease in surface activity of the

component dissolved in water. A certain relationship between surface activity and foam formation suggested itself when the solubility of single members of the homologous series was considered. Fig. 5, taken from Bartsch's work, shows that foaming ability in very dilute fatty acid and alcohol solutions increases steadily with increasing surface activity.

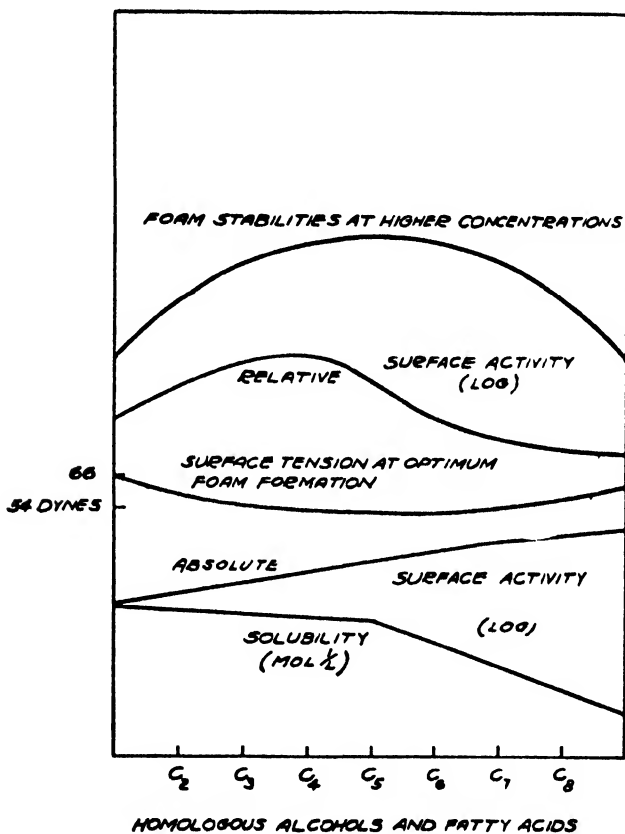


FIG. 5. Scheme of the Relationship between Foam Formation and Surface Activity for Solutions of Higher Concentration.

Solubility and surface activity. When surface-active, foam-forming substances are dissolved partially or completely in molecular dispersion, solubility of the molecularly dispersed substance also plays a certain part in producing foam. Traube and Klein⁶⁷ state that only the molecularly dispersed portion of the solute is related to surface activity; therefore the solubility factor must also be considered in foaming. Solubility decreases with increase in the number of carbon atoms; thus the higher members of the series have a limited solubility, or are insoluble. On the other hand, Traube's rule indicates that capillary activity increases in ascending homologous series. Therefore, the decrease in solubility limits

the increase in surface activity. This fact led Bartsch to assume that the maximum solubility is reached by the lowest members of the homologous series and the maximum capillary activity by the highest members. Therefore, a favorable relationship should exist between solubility, surface activity, and foaming ability for the respective intermediate members, such as butyric acid or amyl alcohol. In the case of higher members, this relationship appears to be more unfavorable because the solubility decreases more readily than the surface activity increases.

This assumption may be proved by taking into consideration the well-known equation of Szyszkowski, who formulated an empirical expression of the relationship between σ (surface tension) and concentration (c)

$$\Delta = \frac{\sigma_M - \sigma_L}{\sigma_M} = b \ln \left(\frac{c}{k} + 1 \right)$$

where σ_L denotes the surface tension of the solution, σ_M the surface tension of the solvent, and k is a constant.

By means of Szyszkowski's⁶¹ formula, values for surface activity relating to solubility are obtained when the constant k , the reciprocal value of which is a measure of capillary activity, is divided by the amount of surface-active substance in a given volume of solution. The greater the surface activity and the solubility, the smaller the value of the quotient.

The influence of solubility is also quite considerable; thus an increase in the solubility of a substance forming the foam leads to an increase in foaming.³

If a second agent is added to a solution of a capillary-active substance, the foaming ability of the mixture may be improved, depending on the changes occurring in the solubility. If the solubility of the first surface-active substance is increased by the addition of the second, then the foaming ability of the mixture may be greater than that of either of the components. For example, nonylic acid, a weak foam agent, becomes an excellent foam agent in a 60-per cent aqueous ethyl alcohol solution. Other foam agents may bring about a decrease in foam formation. In the following examples it was shown that a decrease in solubility brought about by a second capillary-active substance produced a decrease in foaming. A solution of 0.5 per cent of isoamyl alcohol and 0.1 per cent of benzyl alcohol decreased the duration of the foam from 17 to 9 seconds; a *m*-cresol solution and 0.01 per cent of benzyl alcohol decreased the duration of the foam from 11 to 6 seconds. Maximum foaming was obtained with 29 per cent ethyl alcohol; larger proportions caused a diminution in foaming.

Solubility, spreading, and viscosity. There is another proof of the relationship existing between capillary activity, solubility, and foam formation. Since the solubility of a substance depends on the difference between the attraction of the solute for the solvent and the solute for the solute, it is probable that the work of adhesion minus the work of cohesion, called "spreading coefficient," should also be considered an important

factor in determining solubility. But there is a distinction between "spreading in water" and "solubility." In the case of spreading, the most active or polar part is chiefly involved, whereas, in the case of solubility, the whole molecule is concerned. From this standpoint, it is to be inferred that liquids incapable of spreading upon water are insoluble in water. Therefore, the spreading-solubility relationship should be considered in choosing foam agents.

The classical theories⁴⁴ ascribe the property of film formation, and therefore of foam formation, to two general factors: (1) viscosity, and (2) low surface tension of the liquid from which foam originates. Since many liquids possessing high viscosity and low surface tension do not form sustained films or foams, many mobile aqueous solutions with a surface tension nearly equal to that of pure water are capable of foaming.³⁶ This assumption has proved unsatisfactory. Tickell⁶⁵ observed that gas bubbles liberated from oil upon release of pressure formed a foam. An impure substance containing capillary-active and emulsifying constituents having low surface tension and high viscosity fulfills the requirements for foam formation, according to this investigator. Tickell assumed that low surface tension is necessary for the development of a broad foam surface. Since the capillary-active constituents of an impure complex substance, such as petroleum, may concentrate in the surface films, this condition is satisfied in the case of oils.

The question concerning the distribution of a substance between a solvent and its surface layer has been discussed by Thomson⁶⁴ and Ramsden.⁴⁸ Zawidski⁷³ measured aqueous acid solutions to which a sufficient percentage of saponin had been added to insure a stable foam on shaking. He proved that the composition of the solution differed from that of its surface layer, the concentration of the saponin in the surface layer being greater than that in the interior of the solution. This fact agrees with the viscosity and tension relation of aqueous saponin bubbles investigated by Plateau. Under similar experimental conditions, the ratio of concentration of saponin in the foam to that in the solution is not constant. When air is led through an aqueous saponin solution and the foam formed is removed after a certain interval of time, the solution ceases to produce foam, while the foaming ability is definitely increased in a condensed foam; therefore, it is apparent that all the saponin is carried away by the foam. Zawidski ascertained this phenomenon by refractometric measurements. He also observed a second phenomenon, namely, that when alcohol is added gradually to an aqueous solution of saponin a certain point is reached at which the ability to form foam on shaking is destroyed. Zawidski explained this phenomenon by stating that alcohol diminishes the surface tension of water much more than that of saponin. This phenomenon of destroying the ability to form foam was also observed when solutions of isobutyric acid were added to water, thus greatly diminishing its surface tension. Even a large addition of saponin did not produce a stable foam in this case, but a stable foam was obtained by neutralizing the acid with a base.

On the other hand, it was found that if a capillary-active substance was added to a certain foaming liquid like soap, its ability to foam was maintained if the capillary-active substance had the property of forming surface films or skins.

Boundary heterogeneity. Shorter⁵⁹ ascribed the foaming ability of a liquid to the existence of a surface pellicle which was thought to be formed from the dissolved substance. This most fruitful idea of the heterogeneity of the surface layers of a solution was treated theoretically by Gibbs. He proved from thermodynamic considerations that if the addition of a solute lowered the surface tension of the solvent, the solute existed in a higher degree of concentration in the surface layers than in the solution. The decrease in the surface tension is nothing more than positive adsorption and excess concentration in the surface toward the solution:

$$x = - \frac{c}{RT} \frac{\partial \sigma}{\partial c}$$

where c denotes the concentration of the solution, R and T are constants, and $\partial \sigma$ is the surface tension decrease.

This deduction of Gibbs was verified by a number of investigators. Lewis³⁴ measured the surface excess of various solutes in the case of the interface between various solutions and hydrocarbon oils and found in nearly all cases that the measured excess was very much larger than the theoretical value. Thus in the case of a solution of sodium glycocholate the measured surface excess was found to be 5.4×10^{-6} g per sq cm, while the theoretical value was 7.0×10^{-8} g per sq cm. Shorter explained this discrepancy as follows: Gibbs' theory is applicable to cases in which the process of formation of the surface layer is a simple reversible effect, whereas Shorter's experiments on surface layers formed by solutions of saponin, peptones, and albumin showed that the process is thermodynamically irreversible, and therefore beyond the scope of Gibbs' theory. Bartsch's investigations showed that the maximum of foam-forming, surface-active substances depends considerably on the abrupt drop in the concentration, and that this does not apply to skin-forming substances. Surface tension-concentration curves of aqueous solutions for surface-active substances revealed that the foam-forming concentration coincides with the interval of the steep part of the curve; and, conversely, the steep part of the curve indicates that a concentration excess in the Gibbs layer is relatively large for these concentration intervals. This maximum for foaming ability is reached for aqueous surface-active substances when the concentration difference in the boundary layer has a maximum value. In the case of skin-forming substances, the concentration excess in the Gibbs layer, as a result of gel formation, is considerable, and the concentration drop between the layer and the solution is very steep.

Regarding the structure of the Gibbs layer at the maximum of foam formation, two cases deserve consideration: (1) When concentration is infinitely small, the Gibbs layer is composed of water molecules. (2)

When concentration is infinitely large, *i.e.*, saturated, the Gibbs layer consists of molecules of surface-active substances.

These two extremes, in which the boundary layer is homogeneous with reference to the types of molecules, do not induce foaming. In all intermediate cases, in which this layer is made up of two types of molecules and is therefore heterogeneous, foaming occurs. The foaming ability of very dilute or very concentrated solutions having homogeneous boundary layers is small because in the first, water molecules, and in the second, surface-active molecules, predominate. Thus the foaming ability increases when the boundary layer becomes heterogeneous.³ From this standpoint, the addition of a second surface-active substance makes the foam less stable. When this addition causes an increase in surface-active molecules in the boundary layer due to the presence of water molecules, the second substance increases the homogeneity in relation to the molecules of the surface-active substance already present and as a result of which the foaming ability decreases.

The decrease in foaming in the case of high molecular members of the homologous series with increasing tendency toward colloidal solubility is explained by smaller heterogeneity due to the formation of large homogeneous molecular aggregates. The molecularly dispersed members of the series have a greater heterogeneity in the Gibbs layer than the corresponding members which are partially colloiddally dissolved. From this viewpoint, solutions of surface-active substances foam better the more abrupt the concentration drop between the Gibbs layer and the solution, as mentioned previously, and the more heterogeneous the Gibbs layer involved.⁵⁹ High surface activity, low molecular solubility, and homogeneous boundary layers favor abruptness in the concentration drop.³ Only in intermediate members of the homologous series do both conditions exist.

With respect to colloiddally soluble organic liquids, like oleic acid, turpentine, etc., it is assumed that only those capable of spreading on a water surface act as foam formers. The velocity of spreading is not parallel to the rate of surface increase in the formation of homogeneous layers; therefore there is no possibility of the formation of homogeneous layers, and the foam walls consist of heterogeneous boundary layers (molecules of water and organic substances).

Iliin,²⁷ discussing adsorption and superficial energy at the boundary of various phases, points out that a substance dissolved in water is called active when a slight change in its concentration (*c*) greatly changes the surface tension at the air/solution boundary, and that the measure of the activity of the dissolved substance taken in the sense of surface tension (surface activity) is expressed by the equation:

$$g = \frac{\partial \sigma}{\partial c}$$

Neither the activity of an adsorbent, nor the activity of a dissolved substance is involved in Iliin's concept, but only the mutual phase

activity of two or more phases at their boundary. As activity, the gradient of certain energy effects, depending upon the change of one of the variables, especially concentration, is envisioned. Consequently, a gas which has a relatively small adsorption heat and adsorption activity at the same time shows great change in σ ,—a great surface activity as a result of the difference between surface tension of the gas and the adsorbent. Ramsden⁵⁰ indicates that adsorbed molecules in a foam are held in direct contact with both gas and water. There is evidence that before adsorption becomes too great every molecule of the foam agent entering into the surface region is forced to the actual interface and, although still soluble, is retained there permanently.

Shorter,⁵⁸ in his article "On a Classification of Foaming Solutions," states that in order for solutions to be able to form foams they must have a surface tension capable of local variations. This property is due to the existence of a pellicle called the Gibbs layer. Differences in the foaming nature of various solutions considered important by Shorter are not the same as those pointed out earlier by Plateau. Shorter's classification of foam solutions is based upon two distinct points to be considered with respect to the foaming phenomenon: (1) the nature of the process of the formation of the surface layer, and (2) the manner in which the surface layer contributes to the stability of the liquid film.

The process of the formation of the surface layer varies in different solutions. In the case of a mixture of acetic acid and water, equilibrium between surface layers and the solution itself is obtained readily, except in very dilute solutions, so that the process of the formation of the surface layer may be thermodynamically reversible.¹⁰ In soap and saponin solutions, the process assumes another nature. Millner⁴⁰ observed in solutions of sodium oleate an irreversibility of the formation of the surface layer. In working with solutions of saponin, peptone, and albumin, Shorter⁵⁷ showed that the formation of a surface layer proceeds for several weeks without indication of an equilibrium. The substance forming the surface layer separates from the body of the solution at a rate independent of the thickness of the surface layer, and continues to separate for some time without any sign of equilibrium. This process is thermodynamically irreversible, but in albumin solutions, it appears to be "chemically" irreversible, the film substance being insoluble in water.⁴⁰

Shorter classifies foaming solutions into three distinct groups having the following characteristics: (1) Surface concentration thermodynamically reversible; superficial viscosity or rigidity absent. (2) Surface concentration thermodynamically irreversible; superficial viscosity or rigidity absent. (3) Surface concentration thermodynamically irreversible; surface layers especially viscous or rigid.

If the foam-producing agent is a solid body, the spreading and wetting factors are significant. Substances less wetted by water adsorb capillary-active substances from aqueous solutions more readily when building the Gibbs layer. Hydrophobic galena, copper pyrites, and zinc blende are not readily wetted, and therefore pass into foam. Quartz and feldspar

are hydrophilic and, consequently, are well wetted; therefore they remain in the water when separated from their ores in the flotation process.

Substances like sulfides, insoluble oxides, carbonates, carbon, insoluble sulfates, and metals, in fact all substances, as shown by Reinders,⁵³ which attach themselves to the boundary by distribution between two liquids, or are completely surrounded by a liquid, may be used as foam agents. Reinders and Hoffman⁵⁴ investigated adsorption through adhesion at the liquid/gas interface; the theory of these processes was developed by De Coudres.⁹ When two liquids come into contact with a solid body, one of these liquids may displace the other and surround the solid completely; alternately, each liquid may surround the solid partially, with the formation of an edge angle at the contact surface.

In the first case we have a complete wetting by one of the two liquids; but in the second case only a partial wetting takes place, water/oil occurring when an aqueous suspension of a solid substance is mixed with a second liquid insoluble in water, as in the case of water/oil emulsions. When liquid/gas systems, instead of liquids insoluble in water, are involved, the gas phase is present. When water displaces the gas phase from the surface of the solid particles, the latter are completely wetted by water and no precipitation occurs. When only a partial displacement of the gas phase occurs, with the formation of an edge angle, the solid particles are attracted to the liquid/gas interface and the aqueous surface layer floats freely. Valentiner⁶⁹ showed that a powder may actually float better the larger its edge angle.

Relationships become more complicated when a molecularly or a colloidally dispersed solution comes into contact with gas in the presence of a surface of solid particles, such as a foam-producing agent or a stabilizer.

Surface tensions at phase boundaries lose their characteristic fixed values, which cause homogeneous wetting ability, and become functions of the concentration of the dissolved substance. The relation between adsorption and wetting ability was also investigated by Traube and Kieke,⁶⁶ who found that substances which are not readily wetted by water adsorb caprylic acid from aqueous solutions more readily than substances which are readily wetted by water. The solid phase may also lose its foam-forming ability upon the addition of a substance insoluble in water which wets the solid phase more readily than does water itself (chloroform, for example). Further investigations of Traube and Nishizawa⁶⁸ on the adsorption of caprylic acid on minerals showed a relation existing between wetting ability, adsorption, and flotation.

The process of separating particles of finely ground ore from the particles of gangue by flotation is an application of surface phenomena. This process is based on the fact that mineral sulfides, *e.g.*, galena, are wetted by certain oily liquids, but not by water, whereas particles of quartz are wetted by water and not by other liquids. Therefore, if the finely divided ore is agitated with an oil-water froth, the sulfide particles are preferentially wetted by the oil films surrounding the bubbles of the froth, while the quartz remains in the water phase. The sulfide particles which attach

themselves to the bubbles are floated to the surface by a stream of air and separated from the gangue particles which remain at the bottom of the container. Harkins and Feldman¹⁴ state that since the free surface energy of almost all inorganic solids is high, their work of cohesion is of the same order, and the work of adhesion is also high with reference to practically all liquid substances. Since the work of cohesion in water and organic liquids is generally low, the values of the coefficient of spreading of these liquids upon such solids should generally be high. Therefore, the spreading of these liquids should occur upon such solids when their surfaces are pure.

Among other factors, the spreading ability of liquids forming foams indirectly plays an essential part in determining foam formation. Briefly, these views of the criterion of spreading of one liquid upon the other are as follows:

- (1) According to Lord Rayleigh,⁵² all liquids spread on pure water.
- (2) Liquid *b* spreads on liquid *a* if T_a is greater than $T_b - T_{ab}$, where T_{ab} represents the interfacial tension between two liquids and T_a and T_b the respective surface tensions. Non-spreading conditions exist when T_a is less than $T_c - T_{ab}$.
- (3) According to Langmuir, liquids whose molecules are polar or contain polar groups spread on water.
- (4) According to Harkins, a liquid spreads if its work of surface cohesion W_c is less, and will not spread if its work of surface cohesion W_c is greater than its work of adhesion W_a with respect to the liquid upon which the spreading is to occur.

Harkins¹⁹ developed a spreading coefficient by thermodynamic reasoning, using two hypotheses as a basis. Only large-scale motion is of importance in spreading and only free surface energies are involved. The free energy decrease is $S = \gamma_a - (\gamma_b + \gamma_{ab})$, where γ_{ab} represents the free energy of the interface. The work of adhesion W_a is given by the equation of Dupré as $W_a = \gamma_a + \gamma_b = \gamma_{ab}$. The work of cohesion is $W_c = 2\gamma_b$. A combination of three equations $S = W_a - W_c$, indicates that spreading occurs if the adhesion between two liquids is greater than the cohesion in the spreading liquid. Thus positive values of S correspond to spreading, and negative values to non-spreading. In general, Harkins assumes that the value of the coefficient increases as the electromagnetic field around the molecules becomes more asymmetrical. This is because the work of adhesion toward water is greater in the case of asymmetrical molecules than when symmetrical molecules are involved. This excess work of adhesion of asymmetrical molecules toward water may find its explanation in the rupture of very strong electromagnetic fields, whereas in the case of separating water molecules from water only the weakest fields are ruptured. It is evident from the above that spreading of liquids in the process of foam formation becomes an important factor, especially when solid agents participate in the production of a foam system where forces of adhesion and cohesion come into play.

Conclusions

(1) Capillary-active substances promote foaming at a definite concentration.

(2) An abrupt drop between the concentration of the boundary layer and the solute is a requisite for foaming.

(3) The relation between the solubility and the surface activity of a foamer determines whether it is strong or weak.

(4) Foaming, as a rule, occurs only in the case of a heterogeneous Gibbs layer.

(5) Colloidal solubility does not favor foaming. The formation of large molecular aggregates interferes with the principle of heterogeneity.

Table 1. Stability of Foams According to Observations of Plateau

Substance	Stability	Experimental Conditions
<i>Class I</i>		
Distilled water	{ 1- 7 seconds 1- 12 seconds	Atmosphere saturated with vapor Atmosphere dried with sulfuric acid
Glycerol	- 2 seconds	
Sulfuric acid	1- 28 seconds	Atmosphere dry
Nitric acid	- 1 second	Atmosphere saturated with vapor
Ammonium hydroxide		Atmosphere saturated with vapor
Saturated solution of tartaric acid	1-142 seconds	
Potassium nitrate	- 6 seconds	Atmosphere saturated with water vapor
Sodium carbonate	{ - 26 seconds 1- 30 seconds	Atmosphere saturated with water vapor Atmosphere dried with calcium chloride
<i>Class II</i>		
Olive oil	0- 7 seconds	
Lactic acid	1- 18 seconds	
Acetic acid	0- 8 seconds	Atmosphere saturated with vapor
Turpentine	1- 6 seconds	
Benzene	Maximum -12 seconds	
<i>Class III</i>		
Marseille soap	30 seconds-2 hours	
Domestic soap	{ 5-14 seconds; colorless phase of water vapor; stable about 90 minutes	Atmosphere saturated with vapor
Potassium colophane solution	10- 30 minutes	
Saponin solution	{ 25- 40 minutes; colorless phase; maximum stability, 12 hours	
Albumin solution	{ Many hours; colorless phase; stability may be several days	
Ferrie acetate	{ 15- 30 seconds; colorless phase; maximum stability, about 24 hours	

(6) The Gibbs layer in foam systems may differ with respect to the establishment of a state of equilibrium. A distinction is made between thermodynamic and chemical irreversibilities.

(7) The wetting and spreading factors are especially emphasized if the foamer is a solid. Substances less wetted by water adsorb capillary-active substances from aqueous solutions to a greater degree.

The Stability of Foam Systems

Although foam systems are closely related in their properties to emulsions, they differ greatly in their stability. The life of foams is short in comparison with the life of emulsions. Foams are rather labile formations because in other dispersion systems a true static equilibrium is possible—the kinetic energy of molecules creates a considerable opposing action. This kinetic resistance is absent in foam systems.

Table 2. Maximum Foam Duration for Various Substances

Aqueous Solutions of	Optimum Concentration (moles per liter)	Maximum Foam Duration (seconds)
Propionic acid	0.26	11.0
Lactic acid	1.00	7.5
Propyl alcohol	0.34	11.0
Glycol	6.00	1.5
Glycerol	6.00	3.0
Cane sugar	0.50	0.5
Ethyl alcohol	0.28	5.0
Propyl alcohol	0.34	11.0
Isobutyl alcohol	0.09	12.0
Isoamyl alcohol	0.036	17.0
<i>tert.</i> -Amyl alcohol	0.034	10.0
Heptyl alcohol	0.0007	8.0
Octyl alcohol	0.0003	5.0
Formic acid	0.45	4.0
Acetic acid	0.20	8.0
Propionic acid	0.25	11.0
Butyric acid	1.00	18.0
Valeric acid	0.015	9.0
Caproic acid	0.0075	13.0
Heptylic acid	0.0015	16.0
Caprylic acid	0.00025	12.0
Nonylic acid	0.00007	5.0
Ethylamine	0.40	12.0
Aniline	0.10	11.0
<i>p</i> -Toluidine	0.04	6.0
Phenol	0.10	12.0
Benzyl alcohol	0.10	10.0
<i>m</i> -Cresol	0.025	9.0
Nitrobenzene	0.005	6.0
Benzene	0.2
Acetaldoxime	0.37	10.0
Paraldehyde	0.03	9.0
Acetone	0.50	2.5
Methyl propyl ketone	0.05	3.0
Ethyl propionate	0.01	2.5

Table 3. Maximum Foam Duration for Various Substances

Aqueous Solutions of	Maximum Foam Duration (seconds)	Concentration at Maximum Foam Duration (mole per liter)	Surface Tension of Solutions at Maximum Foam Duration (dynes)
Ethyl alcohol	5	0.28	66
Propyl alcohol	11	0.32	56
Isobutyl alcohol	12	0.09	56
Isoamyl alcohol	17	0.036	54
<i>tert.</i> -Amyl alcohol	10	0.034	61
Heptyl alcohol	8	0.0007	68
Octyl alcohol	5	0.0003	64
Formic acid	4	0.45	70
Acetic acid	8	0.20	69
Propionic acid	11	0.25	61
Butyric acid	18	1.0	33
Valeric acid	9	0.015	64
Caproic acid	13	0.0075	57
Heptylic acid	16	0.0015	60
Caprylic acid	12	0.00025	66
Nonylic acid	5	0.00007	70
Benzyl alcohol	10	0.1	59
<i>m</i> -Cresol	9	0.025	62
Aniline	11	0.1	62
<i>p</i> -Toluidine	6	0.04	63

On the other hand, combined with a much greater surface increase, foam formation greatly opposes the tendency of the system to reach a stable state by diminution of the surface, with a resulting decrease in surface tension. But this surface tension decrease is subjected to lasting changes in time, and this is the cause of its having a dynamic, not a static, equilibrium.

The work of Plateau contains experimental data with respect to the duration of foams from various foaming solutions; these are summarized in Table 1.

Recently the relation between foam duration and surface activity was studied; the results showed that an increase in foam duration is parallel with an increase in surface activity.³ This was the case with fatty acids up to butyric, and with alcohols up to isoamyl. Maximum foam duration for fatty acids and alcohols is presented in Tables 2 and 3 (experiments by Bartsch). The surface tension of aqueous solutions compared by Bartsch, using a concentration corresponding to the maximum foaming ability as a criterion, shows great deviations accounted for by isocapillarity of the surface-active substances.

Factors in the Stabilization of Foam Systems

With regard to factors influencing the permanence of a foam, a similarity to emulsions is evident, although the degree of stability is less.

The following factors govern the conditions under which an emulsion system becomes stable, namely, low interfacial tension, optimum concentration, viscosity, behavior with electrolytes, action of protective colloids, presence of a foam agent, existence of a Gibbs adsorption layer and its

thickness, and lastly orientation of molecules in the foam interface. There is also a certain peculiarity in the behavior of foam systems, as compared with emulsions, which may be attributed to their difference in character. As mentioned above, from a purely thermodynamic standpoint it follows that foams cannot be as stable as emulsions. Electrical forces contributing to the stability of emulsions are not so important in the case of foams, where capillary forces apparently play a greater part. The dispersion factor does not act in the same direction in foams as in emulsions.

Foam systems may be differentiated as follows³:

(1) Those originating by shaking water and surface-active organic substances (two-phase foam systems).

(2) Those obtained by shaking emulsions of organic substances, as well as lyophilic foams (three-phase foam systems).

(3) Those systems in which the foam agent is a colloiddally dissolved phase and acts as an integral part of the dispersion medium in the foam system, so that it cannot be distinguished from two-phase foams in which the molecularly dissolved foaming agent is also an integral part of the dispersion medium.

(4) Those in which a solid phase is present occurring as an independent component of the system and in macroscopic quantities similar to the gas phase.

To comprehend the measurable stability of foam systems, those systems must first be considered in which the foam agent is present as an electrolyte, molecularly or colloiddally dispersed, as a protective colloid, or as a solid foam former. In this regard a certain analogy may be drawn between foams and emulsions. Permanent foams, as well as permanent emulsions, under ordinary conditions of temperature and pressure are obtained by using foaming and emulsifying agents. Further, the degree of stability of a foam depends upon the nature of the components participating in the system and whether or not foam originates by shaking solutions of lyophilic or lyophobic substances. While the first foam systems are more stable and less sensitive to added electrolytes (analogous to lyophilic sols), the lyophobic substances render the foams unstable and are very sensitive to electrolytes.

The influence of electrolytes. Lyophilic foams have more outstanding properties, such as viscosity and elasticity, and the influence of electrolytes is so small that in most cases it cannot be proved. This phenomenon is explained by Bartsch by the fact that the foam walls of these systems consist not of the sol, but of the coagulated sol or gel of the lyophilic colloid, as shown by Ramsden and others. The dispersion medium is in a rigid or semi-rigid state, which acts opposite to the change in dispersion so that no precipitation by electrolytes may be expected. Such foam systems may be sensitized by means of surface-active substances. Bartsch proved experimentally that foam formed by shaking a 0.001 per cent saponin solution, after the addition of 0.5 per cent of iso-amyl alcohol, was found to be sensitive to electrolytes. The behavior of

unstable foams with respect to electrolytes is similar to that of lyophobic sols. The only difference is the time of stability; lyophobic sols are stable when compared to lyophobic foams. The speed of coagulation caused by mechanical changes occurring in foam walls is frequently so high that it exceeds the speed of precipitation by electrolytes. Some of these foams are sufficiently permanent that they undergo only coagulation induced by electrolytes. Foam duration is usually expressed in the number of seconds from the moment of interruption of shaking of the foam-forming liquid to the complete disappearance of the foam formed. Bartsch investigated foam systems of amyl alcohol, quinoline, turpentine, and eucalyptus oil. The similarity between lyophobic sols and lyophobic foams is obvious from an investigation of the influence of hydroxyl ions on the stability of foams. Hydroxyl ions were found to increase considerably the stability of foam systems, and to decrease the number of foam bubbles, increasing the degree of dispersion of the gas phase. On the other hand, hydroxyl ions had a peptizing effect upon the foam system, but this action was limited by the degree of concentration. Bartsch's investigation proved that the duration of a foam formed from an isoamyl alcohol solution was decreased from 18 to 15 seconds by the addition of the following concentrations of electrolytes:

Electrolyte	Millimoles per Liter
NaOH	30.0
NaCl	1.0
Na ₂ SO ₄ /2	0.8
H ₂ SO ₄ /2	0.04
BaCl ₂	0.05
AlCl ₃	0.0005

The stability threshold displacement for various electrolytes is pronounced.

Potassium carbonate and potassium citrate were found to be excellent peptizers. Although peptizing action is also a function of concentration, Whitney and Straw⁷¹ found that for peptizing emulsions the favorable concentration lies between 0.2 and 80 millimoles per liter; foam systems show an optimum action at concentrations of 0.1 to 10 millimoles per liter.

The action of protective colloids. Further analogy between lyophobic foams and lyophobic sols is found in their behavior with respect to the action of protective colloids. The influence of protective colloids upon the stability of foam systems has also been discussed and proved experimentally by Bartsch. Lyophobic foam systems may be protected from the precipitating action of electrolytes by protective colloids. The actual concentration of the protective colloid in a foam system is doubtful and differs from that of the starting solution. On account of the decreasing surface tension, lyophilic colloids gather at the boundary surface of the solution. The presence of these substances in a foam is shown by an increase in its stability. Approximately equal proportions of various

protective colloids are necessary to increase foam duration to the same extent. Bartsch found that the lower the concentration, the more surface-active is the protective colloid. Very strongly surface-active substances show an extreme deviation (Refer to Table 12 in the paper by Bartsch³). The relative protective number for foams with respect to the sequence of the protective action was found to be in complete agreement with that of gold numbers for the same protective colloids. A protective colloid may act on a foam system in a direction opposite to the one mentioned above. Since precipitation in the interface is considered a fundamental condition for the formation of a three-phase foam system, it seems reasonable to assume that those protective colloids which prevent this precipitation make the formation of three-phase foam systems impossible. The protective colloids at certain concentrations completely displace the solid phase from the foam system, and in this case an unstable two-phase foam system is formed instead of a three-phase. The alternative explanation favored by Bartsch is that a stable two-phase system develops when the protective colloid is present in the solution in a high enough concentration, because protective colloids themselves are able to build up a stable two-phase foam system. Flotation practice makes use of this phenomenon in determining the behavior of various ores against certain protective colloids by measuring the weighed amounts of the corresponding ores which may still be adsorbed by the foam at equal concentrations of the colloid.

Viscosity as a factor in the stabilization of foam systems. Bartsch also worked out the idea of increasing the stability of foams by adding substances to increase the viscosity. He carried out experiments with isoamyl alcohol solutions to which various percentages of glycol and glycerol were added. The result was that only very high concentrations of about 60 per cent increased the stability markedly. This was explained by the action of the "removal law" of Michaelis and Rona,³⁹ according to which glycerol or glycol was partially removed from the foam walls by the presence of surface-active substances. A soap-saponin solution may serve as an example of the "law of removal." In this case, the soap solution has a lower surface tension than the saponin solution, and this results in the removal of soap from the interface by saponin. The fact that a saponin solution loses its ability to form a stable foam on the addition of alcohol may be partially explained by the same removal process; but, on the other hand, it is essential that saponin be really soluble in alcoholic solutions and that it does not form skins.

Quincke⁴⁷ was the first to describe the peculiar phenomenon that ethyl ether, present even in small amounts in the surrounding atmosphere, destroys the foam of a good foaming liquid. Again, the capillary-active ether removes the foam agent in the liquid. The skin-forming, abnormally adsorbed substances, such as soap, saponin, lyophilic foam agents (albumin and gelatin), the adsorption of which is not influenced by capillary-active substances taken in minute amounts, may increase considerably the stability of isoamyl alcohol foam; 0.000001 per cent of soap increases the foam stability twofold, whereas 0.001 per cent of gelatin is

required for the same action. This depends on the surface activity of the corresponding substances. Stability also depends to a certain extent on whether the foam contains large or small bubbles, and whether the bubbles are elastic or rigid. Certain substances added to a foam-forming solution not only increase the stability by increasing the viscosity, but impart a certain elasticity by softening the interface skins, thereby preventing the coalescence of bubbles in a foam.

Boys⁶ reports an experiment in which one drop of a soap solution added to 30 g of a saponin solution was sufficient to prevent the rigidity of saponin bubbles. On the addition of three drops, the surface skin became movable and elastic, as in the case of pure soap solutions. Glycerol added to a soap solution induces foaming, increases viscosity, and, at the same time, assists in the formation of soft and flexible skins. Therefore, the behavior of saponin solutions with glycerol resembles that of pure soap solutions. Elastic foams and those with large bubbles appear to be more stable. It is probable that an explanation for the stability of durable foams as, for example, those produced by the sea, by beer, or by aqueous solutions of saponin and soap, must be sought partially in the formation of very viscous, semi-rigid or gel-like membranes at the interface. Wheat gum used in the beer industry, as well as other dextrin-like substances, acts like glycerol, increasing the viscosity and producing softer and more elastic skins. That the various degrees of stability of a foam often depend on the properties of the bubbles forming the foam has been proved. Whether the bubbles are elastic or rigid depends chiefly on the nature of the films. Soap solutions are distinguished by the formation of very elastic bubbles, which show a smooth, flexible surface. On the other hand, bubbles of saponin solutions are much more rigid; when a bubble collapses, a pleated sac is observed. The difference between the elastic lamina of soap and the rigid type of saponin becomes evident from the rearrangement in colors which takes place with a continuous change in the thickness of the lamina. In saponin foams, the laminae are so rigid that certain color spots are retained unaltered upon a given lamina. In the tendency toward equilibrium, some laminae burst or unite to form new ones. But still the history of the laminae in question may be read from these invariable color spots.

The action of finely divided solids. While the behavior of gas/liquid and liquid/liquid systems in themselves is evidently different, nevertheless certain analogies are found. Both emulsion and foam systems may be stabilized, not only with agents which are molecularly or colloiddally dissolved, but with finely divided solids, first applied by Pickering to emulsion systems. The latter may replace solutions in the interface and build up a boundary layer to increase the stability of these systems. Donnan,¹¹ speaking of the stability of foam, states: "If air is violently churned up with water, only comparatively large bubbles are produced and these quickly rise to the surface and burst. If a very small amount of a substance which concentrates at the air/water interface is added, an almost milk-white air emulsion of small bubbles is produced which rise to

the surface and produce a relatively durable froth." According to Lord Rayleigh,⁶¹ who discussed this phenomenon, it is clear that diminution of interfacial tension facilitates the subdivision or the dispersal of air. The existence of the surface layer imparts a certain amount of stability to the resulting foam, since it gives rise to forces which resist the thinning of a bubble wall. Any sudden increase in the surface produces a momentary diminution in the concentration or thickness of the interface layer and hence an increase in surface tension, which persists until the normal thickness or concentration is readjusted by diffusion of molecules from the inside volume—a process which in very dilute solutions occupies a perceptible time. That this explanation of Lord Rayleigh is correct, says Donnan, may be seen from the fact that very often stronger solutions of the same surface-active substance would not foam at all. In this case the readjustment of the equilibrium thickness or concentration in the gas/liquid interface occurs with such rapidity that practically no rise in surface tension, and hence no counteracting force, comes into play.²⁴ On the other hand, in the case of higher concentrations, aggregates of gas bubbles and solid particles can no longer be formed by shaking, because the interfaces thus formed are already occupied by molecules of the surface-active substance.

Dynamic equilibrium² established between the speed of formation of the adsorbed layers of the foam-forming agent or stabilizer at the solid/liquid boundary on one side and the speed of such layer formation at the gas/liquid interface on the other side determines to a certain extent the stability of this three-phase foam system in the case of higher concentrations of the foam agent. As has been demonstrated in the experiments of Hoffmann²⁵ and others, small solid particles may contribute to the stabilization of a froth or foam, as in the case of the mineralized frothers or the ore flotation process by the preferential aggregation in the interface between two phases. Bechold, Dede, and Reinders⁴ state that solids prevent coalescence of bubbles in foams, as well as in emulsions. Solids prevent coalescence of droplets, thus increasing the stability of a system. The degree of dispersion of the solid was found to be of even greater significance in foam systems than in emulsions. Substances in a very fine degree of division increase the foam stability much more than substances of a coarse grain division. There is an optimum dispersion of the solid phase for the stabilization action between colloidal and coarse division.² For example, when lead glance which has been passed through a 900-2500-mesh sieve is used as a foam agent, it increases foam stability to 60 seconds; when lead glance which has been passed through a 9000-12,000-mesh sieve is used as a foam agent, the life of the foam formed is increased to several hours. Further, the proportion of the stabilizer, whether it is a liquid acting as a foam-former or a solid, is decisive for the formation of a stable foam. The magnitude and stability of aggregates of gas bubbles and solid particles are determined by the concentration of the foam agent, and the nature and affinity of the foamer and the solvent for the solid phase.

Forces Involved in Maintaining Stability

Electrostatic and capillary forces. Among the forces involved in maintaining the stability of a foam system are electrostatic and capillary forces. Concerning the nature of forces producing an attraction between solid particles and a gas, it is known that all components of a three-phase foam system are charged with electricity of the same sign, gas bubbles being charged negatively against water; therefore stability depends on the valence and the adsorption ability of the cations. The electric influences are indirect rather than direct, and seem to determine only which boundary phase the particles may enter and the degree to which they may coagulate and change the structure of the foam. The charge of the gas phase may be determined by the indirect method, using the ion precipitation series of colloid chemistry. Cations induce precipitation in various foam systems, according to their valence, and these systems have been found to be negatively charged. Bartsch determined the charge on a gas bubble in a foam system, but the potential drop at different boundaries in the system has not been proved. It is still undecided whether electrokinetic potentials or phase boundary forces are involved. Where gases are concerned, the balloelectric effect should be considered. The fuzzing effect of Lenard^{15,33} is based upon a similar phenomenon fundamental to balloelectricity. A balloelectric effect occurs when gas bubbles pass through a liquid and then leave the surface. The electric energy from the double-layer reaches the gas phase and gives it a certain charge. Balloelectricity implies streaming potentials, but in this case the charges at the boundary of the liquid (gas) move readily; therefore, not a displacement, as in the case of streaming potentials, but rather a destruction of the double-layer by the tangentially-acting mechanical forces takes place, and the electricity carried by both layers (external and internal) reaches the gas. The gas phase was found to be negative, while electrolytes, acids, and certain active substances⁸ produce a change in the charge even for small concentrations. In general, electric influences in foam systems have not as yet been thoroughly investigated.

Taggart⁶² studied the changes of the potential under the influence of electrolytes. He permitted a small gas bubble to migrate cataphoretically around the longitudinal axis of a rotating glass cylinder between two electrodes and determined the direction of migration and its speed under various conditions. He found that the gas bubble in pure water was charged negatively. The velocity of air, oxygen, and hydrogen spheres in water was found to be about 4×10^{-4} cm per second per volt per centimeter. The presence of hydrogen ions decreased the boundary phase potential to zero without a change in the sign of the charge. Tri- and tetra-valent cations caused a change in the sign of the charge. A sphere of gas in a solution was found to change the sign of its charge as it diminished in size by being adsorbed into the solution. Surface-active substances decreased the cataphoretic speed according to Traube's rule. In general, interfacial potential differences are of great importance and play a fundamental part in determining the stability or instability of the col-

loidal state of matter. In the case of foam interfaces, potential differences are not perhaps of such great importance, but since very little work has been done in this direction, our opinions as to the importance of this factor must be held in abeyance.

It has been shown only in the case of an air/water surface that an electric separation or potential difference exists in the interface layer, and that certain substances can produce pronounced variations or even reversal in sign of this electric double-layer. There may be a possibility for direct measurement of the potential drop between single phases of a foam system using the Haber-Klementschevitch glass electrode. The influence of charge upon attraction between components of a foam system is marked only in case other forces, such as capillary forces, are weak. The fact that gas bubbles adhere to solid particles in spite of electrostatic repulsion of the components indicates that the more powerful capillary forces participate to a great extent in maintaining permanence.

The coalescence of two drops takes place at the boundary partition, where a diminution of surface occurs and where capillary forces originate, which tend to tear apart these boundary sections and to counteract their coalescence. Capillary forces act against molecular attraction—a cohesion between molecules when molecules of the same kind are present and an adhesion when different ones are involved. These forces existing between molecules of similar and different natures, more than the electric elementary forces, must be considered in the case of three-phase foam systems.

Talmud and Suchowolskaja,⁶³ in their investigation of elementary foams, pointed out that stability depends rather on the degree of hydration, and that the slipping velocity of the water layers in the walls of laminae is a determining factor in stability because substances stabilize before the adsorption layer is obtained.

The adsorption layer in the interface of a foam system and its thickness as a factor influencing stability: the Langmuir-Harkins orientation theory. As in the case of emulsion systems, so in three-phase foam systems—for example, amyl alcohol, solid agent (foamer), oleic acid (stabilizer)—a relationship appears to exist between stability, the presence of an interfacial layer, and its thickness.

Adsorbed molecules are held in direct contact with both gas and water in a foam system. Some adsorption surfaces are extremely viscous or even rigid (saponin and nearly all proteins), and the adsorbed particles are in mutual contact. Others are freely mobile (quinine and soaps), and the particles are either more widely spaced or so oriented that only cohesion between liquids comes into play. In many cases where adequately permanent bubble films are obtainable, the interference colors developed as the film becomes thinner are disposed in horizontal bands when the surfaces are mobile, but chaotically disposed when the surfaces are rigid.

It is known that gases or vapors can be condensed or adsorbed by solid and liquid surfaces. The question arises whether the formation of primary monomolecular films ever occurs in such cases. Langmuir³⁰ mea-

sured the adsorption of a number of gases at low temperatures and pressures on defined surfaces of mica and glass and concluded that the maximum quantities adsorbed are always somewhat less than the amounts to be expected in a monomolecular surface layer. Carver⁷ found similar results measuring the adsorption of toluene vapor on known glass surfaces.

This view that the maximum adsorption from the gas phase cannot exceed a monomolecular layer has, however, been much criticized. Thus Evans and George,¹³ on the basis of their own measurements of the adsorption of gases on a known surface of glass wool combined with data obtained by Mulfarth,⁴² concluded that the adsorption layer may be several molecules thick. Reference may also be made to an article by Wilson,⁷² who deduced from the results of the adsorption of oxygen and nitrogen at low temperatures that these gases are held in layers several molecules thick.

Another type of surface-layer formation is at the surface of liquids where a substance dissolved in a liquid concentrates preferably at the liquid/air or liquid/vapor interface. Gibbs,¹⁶ and later Thomson,⁶⁴ showed that if a dissolved substance (in relatively dilute solution) lowers surface tension, it will concentrate at the surface. That such a phenomenon actually occurs in foam has been demonstrated qualitatively in the experiments of Hall,¹⁸ Zawidski,⁷³ and Kendrick and Benson. If various experimental values are considered, evidence is produced that they are not materially different from those found by Langmuir and Adams for the oriented monomolecular layer of practically insoluble fatty acids resting on the surface of the water. Harkins' theory, regarding monomolecular films produced on water, points out that these films occur only when the spreading coefficient has a relatively high value. Since these high values result only when the spreading substance contains a polar group in its molecule, the presence of such a group is essential to a monomolecular film for spreading on water, but not at all essential for the formation of a thicker film. Donnan explained the fact that the thickness values in some cases are greater by the partially or completely vaporized state of the adsorption layers.

Adams and Marcelin¹ made the important discovery that the monomolecular surface films which they investigated may pass rapidly, on increase in temperature, from the state of solid or liquid surface films to the state of vaporized surface films in which the "juxtaposed" molecules become detached from one another and move about with a Brownian or quasi-molecular motion. These investigators attributed this behavior to the thermal agitation of the water molecules to which they were attached. Bartsch first emphasized the fact that the stability of three-phase foam systems, analogous to three-phase emulsion systems, depends upon the dimensions of the adsorbed Gibbs layer of the stabilizer. He calculated the thickness of the adsorbed layer from data obtained for the weight of the solid phase, the specific gravity of the solid phase, and the size of the particle given by the degree of dispersion, and found that the adsorbed layer under stable conditions may run up to five to ten molecules thick

with a layer of galena, two molecules with copper pyrites, and five to seven molecules with zinc blende.

This calculation does not consider the fact that the adsorbed surface is actually much larger than the calculated surface of particles because of possible rupture of the adsorbed surface. Also, a quantitative adsorption has been assumed, whereas it follows from these determinations that in very dilute oleic acid solutions the adsorption was relatively less than in concentrated solutions. Adsorption of oleic acid at the boundary surfaces of air bubbles was not accounted for. The stability of three-phase foam systems is a function of the foaming agent or stabilizer, that is, the power of adhesion between solid particles and air bubbles is determined by the adsorption layer. In order to render three-phase foam systems stable, the thickness of the solid layer or the oleic acid concentration should be such that the surface of the solid phase is covered with a layer of oleic acid; this surface layer has none of the properties of oleic acid as a whole. Since the thickness of the layer considered was less than four molecules in diameter, the probability of a monomolecular layer was assumed. Beyond the optimum thickness, the bond between solid particles and air bubbles is weakened and the stability of the system decreased. Freundlich,¹⁵ discussing the action of solids upon foams, explains the resistance ability of the foam structure against solids as follows: when a solid is wetted by such solutions as soaps and saponin, it is "sucked" into the edge canals which are rich in liquid without destroying the structure of the foam externally.

Bartsch has defined conditions for the stability of a foam, taking into consideration the orientation theory of Langmuir³¹ and Harkins.²¹

The orientation theory postulates that molecules in the interfacial layer assume a definite direction. The atomic groups (carboxyl and oxy-amido) of a molecule rich in residual valences are so placed that almost complete saturation occurs in the boundary. When the boundary is not saturated by any residual valences, the molecule directs the most saturated atomic group to this boundary, that is, the carboxyl group of oleic acid is directed toward the solid phase, and the methyl group is directed toward the outside. When a methyl group comes into contact with a water/air boundary, it displaces the water molecules from the boundary layer because the interfacial surface tension in the presence of the methyl group is decreased, i.e., the water molecules are subjected to the expelling influence of the carboxyl group when competing for the surface of the solid phase.

The energy of the interface has a tendency to reach the lowest possible value, and this is the force which causes cohesion of solid particles to air bubbles. When only one molecular layer of oleic acid is present between air bubbles and solid particles, the intensity of adhesion is produced by the stronger forces existing between the residual valences of the solid phase surface and the forces of the carboxyl groups of the oleic acid. The latter forces are essentially greater than the forces of cohesion acting between the oleic acid molecules, as shown by Harkins. In the case of

octane, the entrance of an oxygen atom into the molecule increases its cohesion up to 2 per cent, while the adhesion to water increases the cohesion up to 65 per cent. But the oleic acid is adsorbed not only by the solid phase, but also by the water/air boundary, depending upon which of the boundaries the oleic acid molecules have been previously adsorbed or, in other words, upon the rate of adsorption for the two boundaries. In the case of oleic acid concentrations which are high enough to surround gas bubbles as well as solid particles with a layer of oleic acid, a certain attraction is always observed. Bartsch explained this as follows: In shaking an oleic acid emulsion with air in the presence of solid particles, the water/air boundary is always renewed. The rate of adsorption of the water/air interface and the rate with which an oleic acid droplet spreads upon the surface of a gas bubble is less than that of adsorption by the solid phase.

The Langmuir concept of spreading, in this case, is based on the attraction existing between carboxyl groups and the molecules of the surface of the water or the surface of the solid phase. This attraction for the surface of a solid phase is greater than that for the surface of water, because the water molecules are displaced by solid particles wetted by oleic acid. The difference between the rate of adsorption and the rate of spreading of the oleic acid at the boundaries is due to the fact that even at higher concentrations of oleic acid the water/air boundary is not completely covered with a closed oleic acid layer, so that there will always exist a possibility of the formation of gas bubble complexes and solid particles. A gas, a liquid, and solid particles, held together by oriented oleic acid layers, comprise stable foams.

A monomolecular layer of oriented oleic acid molecules binds the aqueous solution to the gas and the solid surface, as well as the gas to the solid surface. The relation between the thickness of the interfacial layer and the stability of a foam, according to the orientation theory, may be described thus: as a result of the tendency of the free energy of the interface to acquire the lowest possible value in the case of low concentrations, the intensity of adhesion between solid particles and gas bubbles decreases with a decrease in the number of molecules of the foamer or stabilizer inducing adhesion. The intensity of adhesion between solid particles and gas bubbles is due to saturation of groups of molecules of the stabilizer rich in residual valences. These valences have their origin in the boundaries of the solid phase, as well as in a decrease in surface tension produced by saturated groups of substances in the gas/liquid boundaries.

In the case of high concentrations exceeding the optimum conditions of a state of permanence, the intensity of adhesion is the resultant of cohesion existing between molecules of the foamer in the adsorbed layer which, in this case, is made up of a considerable number of layers of molecules of the adsorbed substance.

The influence of cohesion increases with the number of layers of molecules. Orientation requires asymmetrical molecules; for the most stable form of a system, it is necessary that it have the lowest possible free

energy. Therefore the molecules orient themselves in the interface so that the paraffin hydrocarbon chain remains in the oil, while the active polar group (COOH), which exercises the greatest electromagnetic force, is in the water.

At the surface of the solid phase the molecules of water are subjected to the displacing influence of carboxyl groups; at the water/air boundary, the displacing influence of methyl groups toward oleic acid is exerted.

Conclusions

- (1) Foams are labile formations with kinetic resistance lacking.
- (2) A dynamic, not a static, equilibrium is characteristic of foam systems. A great surface increase in foam formation counteracts stability with a decrease in surface tension.
- (3) The nature of the components of a system determines foam stability; lyophilic foams are more stable than lyophobic.
- (4) The rate of adsorption in the boundary accounts for the stability of foams.
- (5) Some ions may produce a considerable increase in the stability of foam systems, increasing the dispersion of the gas phase, whereas other ions act as peptizing agents.
- (6) For solid foams, foam stability increases with the degree of dispersion.
- (7) High concentrations of substances added to increase the viscosity of a system increase its permanence.
- (8) Certain substances possess the ability to displace foamers from the interface.
- (9) Certain substances, such as glycerol, have a greater influence on the formation of soft and flexible skins than on viscosity. Elastic foams composed of large-size bubbles are considered more stable than those composed of small-sized bubbles; this is not in alignment with other colloidal systems.
- (10) Electrostatic and capillary forces are involved in maintaining the stability of a foam.
- (11) The relation between the thickness of the interfacial layer and stability is analogous to that of emulsion systems. The Langmuir-Harkins orientation theory is applicable to foam systems.

Transition to the Unstable State

Forces Acting in the Thinning of a Film

The interior of films composing foams is subjected to a continuous diminution in thickness by internal currents due to gravity and suction at the edges. The weight of the lamina has the tendency to make it thinner by forcing the molecules to slip continuously from the top to the bottom of the bubble. On the other hand, the liquid between two surface skins of a lamina moves upward very slowly following the force of gravitation. The friction is great because, according to Poiseuille's law, the speed with

which a liquid moves in a capillary is proportional to the fourth power of the radius and is, therefore, extremely small in such a small cross-section.

Liquids behave differently. Gibbs¹⁶ assumed that the motion of the liquid through which a bubble of air is rising is similar to that of a liquid running out from between two surfaces. This motion of the liquid may be greatly retarded by its viscosity as soon as the space between the two surfaces is reduced to the thickness of a lamina. The effect of an increase of the surfaces in increasing their tension becomes greater and more permanent as the quantity of liquid available for supplying the substances forming the increased surfaces becomes less. Gibbs offers a rough estimate of the amount of motion possible in the interior of a liquid lamina with respect to its exterior by calculating the descent of water between parallel vertical planes when the motion of water is reduced to zero. He uses the coefficient of viscosity determined by Helmholtz and Piotrowsky²² and obtains $V = 581D^2$, where V is the mean velocity of water expressed in millimeters per second and D is the distance in millimeters between the fixed planes, which is supposed to be very small in proportion to their other dimensions. For the same temperature, the descent of water in long capillary tubes is $V = 337D^2$, and for descent between parallel planes it is equivalent to $V = 899D^2$. Gibbs draws the conclusion that in a film of a liquid which has a viscosity and a specific gravity not very different from that of water, the mean velocity of the interior relative to the surfaces will probably not exceed $1000D^2$. This is a velocity of 1 mm per second for a thickness of 0.1 mm, 0.6 mm per minute for a thickness of 0.001 mm, corresponding to the interference light of red of the fifth order in a film of water, and 0.036 mm per hour for a thickness of 0.0001 mm, corresponding to white of the first order. Such a small internal current is evidently consistent with great persistence of the film, especially in those cases where the film can exist in a state of the greatest tenuity. On the other hand, Gibbs states that the foregoing equations give so large a value of V for a thickness of 1 mm or 0.1 mm that a film evidently can be formed without drawing up any great weight of liquid, and any such thicknesses as these can have only a momentary existence.

Besides the action of gravity on the interior of a film, another cause produces changes, namely, the edge where the film terminates. At such an edge, there is generally present a liquid mass continuous in phase with the interior of the film bounded by concave surfaces. The pressure at the edge is, therefore, less than that in the interior of the lamina by which its thickness is rapidly reduced. Unless the lamina is very viscous, its decrease in thickness near the edge causes a rapid upward current on each side, while the central portion slowly descends. These processes rapidly reduce the thickness of the film. The volatility of the principal component is another example of the downward tendency of the interior of the film.

If in the case of a film of soap and water the humidity of the surrounding atmosphere is such that the vapor pressure of water at a level between

the top and the bottom of the film has the same value in the atmosphere as in the film, then evaporation takes place in the upper portions and condensation in the lower portions. These processes occasion currents of diffusion, the effect of which is to carry the moisture downward. In the event the vapor pressure of water in the atmosphere differs little from that in the film, the processes described would not be sufficiently rapid to be of importance. But in the case of a film of soap and water in a dry atmosphere, or a film of soap and water with glycerol in a moist atmosphere, the effect of evaporation or condensation is not to be slighted. In the first case, decrease in the thickness of the film is accelerated; in the second, it is retarded. In the case of a film containing glycerol, it is to be expected that the condensed water will not replace the fluid carried down by the internal current, but that a combination of these two processes will tend to remove the glycerol from the film. When a component which greatly diminishes the tension of a film is volatile, the effect of evaporation and condensation may be considerable, even when the mean value of the vapor pressure for that component is the same in the film as in the surrounding atmosphere. Gibbs illustrates this by using two components, S_1 and S_2 , and states that the vapor pressure in a film must vary with the weight Z , since surface tension varies, and these variations almost satisfy the equation:

$$\gamma_1 \frac{\partial \mu}{\partial Z} + \gamma_2 \frac{\partial \mu_2}{\partial Z} = 0$$

γ_1 and γ_2 denoting the densities of the components S_1 and S_2 in the interior of a film. The variation of the potential of S_2 as we pass from one level to another is, therefore, as much more rapid than that of S_1 as its density in the interior of the film is less. If the resistances restraining evaporation, *i.e.*, transmission through the atmosphere and condensation of the two substances, are the same, then these processes will proceed more rapidly with respect to S_2 , and the values of $\frac{\partial \mu}{\partial Z}$ and $\frac{\partial \mu_2}{\partial Z}$ will have opposite signs, the tendency of S_1 being to pass downward and that of S_2 to pass upward. Moreover, the evaporation or condensation of S_2 will produce a much greater effect than evaporation or condensation of the same quantity of S_1 . If condensation of S_2 takes place at the top of the film, it will cause a decrease in surface tension and an expansion in that part of the film by which its thickness is reduced as in evaporation of S_1 .¹⁶

Factors Involved in the Transition to the Unstable State

Thus the general conditions of the persistence of a liquid lamina are such that the substance which causes a decrease in surface tension in the lower parts of the film must not be volatile. Volatility influences rupture, for it is understood that when superficial molecules are lost by evaporation, their intrinsic cohesion must have been very small. In spite of the mobility of the superficial layers, little force is necessary to produce rupture; motion (evaporation) in the external molecules favors rupture.

Plateau, in his theory of foams, assumed that for a liquid to be able to form bubbles, develop a large film and yet be resistant, it is necessary that the viscosity of the superficial layers of the film be sufficiently dense for thinning to occur slowly. But, on the other hand, it is also necessary that the surface tension be relatively weak so that it cannot overcome the opposite resistance of viscosity. Liquids having a high superficial viscosity and a relatively strong surface tension at the same time do not form bubbles. Liquids with a very low superficial viscosity do not form bubbles because the films surrounding them may become extremely thin in a short time, and an external or internal factor may break them. The chances for rupture are considerably less for a liquid having a low viscosity, as the bubbles are larger.

Plateau's principles further indicate that the superficial layer of liquids has a viscosity independent of the interior mass. In certain liquids, the superficial viscosity is greater than the internal viscosity—sometimes to a considerable extent as, for example, in water and in a solution of saponin. In other liquids, on the contrary, the superficial viscosity is weaker than the internal viscosity, as in the case of turpentine and alcohol. The formation of a lamina is the result of the cohesion and viscosity of a liquid. When a lamina develops it progresses in this manner because it is pushed upward continuously by the air; hence it continues to rise. On the other hand, the liquid to which its edges are attracted cannot follow the lamina because of its weight. Therefore this liquid remains behind; but cohesion and viscosity interfere so that no rupture occurs between the lamina formed and the surrounding liquid, the lamina growing until the action exerted upon the outer part of the air bubble has produced its effect. Changes in physical conditions, such as an increase in the temperature of the liquid decreasing capillary pressure, cause the lamina to collapse under a smaller weight. The foam duration of a 0.05 molar aqueous solution of isoamyl alcohol at 50° was found by Bartsch to be 32 per cent lower than that at 18°.

When the superficial layers have a very high viscosity, molecular motion is difficult, and no changes occur in the film before it is affected by surface tension. When sufficiently energetic, surface tension disrupts the film. If a bubble is formed from a glycerol solution and expanded, it gradually changes in thickness before it ruptures. These gradual changes in thickness are visible macroscopically, as indicated by the coloration of the film. In a glycerol solution, the course of the color change is reversed, that is, from red to green of the last order before rupture, owing to the fact that glycerol adsorbs moisture from the air. The action of weight tends to make the film thinner; adsorption on the contrary tends to make it thicker. The course of color change shows that at first thinning has the greatest effect, but that later thickening dominates. There is an interval in the existence of a bubble where these two factors are counterbalanced, that is, a period in which the film gains as much as it loses. If a glycerol solution has a density not exceeding 1.1, it undergoes only a small decrease in density compensated by an increase in fluidity as a result of

dilution with water. Changes in density are not the principal reason for this thinning.

When the film has retained a large proportion of water, the relation between superficial viscosity and surface tension must be sufficiently great to make rupture difficult. On the other hand, because of continued adsorption of water vapor, the film should not become thicker in any phase of its life. These two factors constitute the resistance of the bubble to rupture. Furthermore, if the ratio between superficial viscosity and surface tension increases, but not in proportion to viscosity, it becomes insufficient to maintain permanence, and the bubbles of the foam system collapse. This relation was indicated by Plateau's⁴⁴ experiments (Table 4).

Table 4. Plateau's Experiments

Substance	Superficial Viscosity	Film Tension	Viscosity-Tension Relation
Water	100.00	14.60	6.85
Glycerol	60.42	8.00	7.55
Saturated solution of sodium carbonate	91.14	8.56	10.65
Saturated solution of potassium nitrate	96.35	11.22	8.59
Saturated solution of calcium chloride	90.62	11.06	8.19
Marceille soap solution, 1/40	94.79	5.64	16.81
Domestic soap solution, 1/30	96.35	6.44	14.96
Potassium colophane solution (resin soap obtained by distillation of turpentine)	84.89	7.68	11.05
Saponin solution, 1/100	Extremely high	8.74	Very high (not determined)
Albumin solution	Identical	11.42	Identical

The thinning of a film may be due to small concave surfaces formed along its contour. Thinning is slower for the same contour if the film occupies a larger surface. In the case of equal surfaces, thinning is less. This thinning rate increases with the diameter; but this is not the only factor involved in rupture, because if it were, the resistance of bubbles would increase with size. Usually these two influences compensate each other. A film of a given dimension has the greatest resistance to rupture when it is attached by its contour horizontally in a plane free from evaporation, agitation of air, or vibrations produced by the liquid. Two opposite forces act in a bubble, one centripetal, situated in the colorless part of the film, the other centrifugal, residing in the colored portion of the film with a maximum in the center corresponding to the so-called "black spot." * But apart from any action of the atmosphere, the interior of a fluid film is generally subjected to a continuous diminution in thickness by the internal current due to gravity and suction at the edges; sooner or later the interior ceases to possess the properties of matter as a whole. The film then becomes unstable with respect to the thinnest parts, which tend to become still thinner, owing to an apparent attraction between the

* The black spots never have a thickness (20-40 $m\mu$) corresponding to the gray of the first order. The smallest thickness ever determined for these black spots was 100 $m\mu$ (white of the first order); ordinarily, colors of higher orders are observed (300 $m\mu$).

surfaces of the film, discernible at its extremities, but becoming obvious when the thickness of the film is sufficiently reduced.

Rupture of a film for many liquids cannot always be determined because it is rather sudden, and the intermediate phases of rupture cannot always be observed. However, there are methods for determining the thinning of laminae and for measuring the limiting thickness, which is a measure of the stability of films composing a foam: (1) by tracing the causes of thinning, *i.e.*, gravity and surface tension, and (2) by observing the decrease in thickness produced by a centrifugal force, as shown by Rickenbacher.⁵⁵

Upon a drum rotated around a vertical axis, Rickenbacher spread a film in a horizontal plane and observed the appearance of Newtonian colors, which served as a measure for the decrease in thickness. (The Newtonian interference colors depend upon the interference of light reflected from the anterior and posterior surfaces of the laminae.) By a comparison of the colors observed with Boys' ⁶ table of colors, the apparent thickness of the lamina with an angle of incidence may be determined (the more light reflected, the greater the angle of incidence). Boys' table of factors may also be used in converting apparent into actual thickness.

The process of thinning may be observed to a limited extent in soap/water films. It is apparent that a film whose coloration approaches black exhibits marked instability. The continuous change in color is interrupted only when the black spots make their appearance, spreading rapidly. Decomposition of soap solutions, rendering them opaque, is another reason for film rupture. Precipitation, not an expansion of the film, occurs during the formation of these black spots, and may be attributed to the film's greater thickness at their edge. Black spots apparently are many times thicker than the portion of the film from which they are formed. If the formation of black spots were due to an expansion of the film, it is evident that they would not be present. The thickening of the edge of the film cannot be accounted for by contraction. Expansion of the upper part of the film and contraction of the lower and thicker part would be resisted less by viscosity and favored more by gravity than such expansions and contractions producing the phenomenon described. A rapid formation of a thin spot by an internal current would induce an accumulation at the edge of the material forming the interior of the film.

Van der Willigen ⁷⁰ states that films of alkali solutions are rather unstable because the black zone is formed from the alkali portion of the soap. However, Plateau believes it more probable that soap itself tends to be removed from the solution and out of the colored part of the film. In a much more concentrated solution, it forms the black zone. This opinion is based on Newton's experiments, which proved that dark blue always precedes black and is observed only when the solution contains a high proportion of soap. This led Plateau to assume that the difference in composition between the black zone and other parts of the film is small and the decrease in thickness gradual. The exploding force of a bubble is more intense the greater the proportion of water because the bubble

bursts sooner, disintegrating its components, while, at the same time, the force of contraction has been weakened to the same extent. Conversely, the more soap present the less the intensity and the more energetic the force of contraction. This is to be doubted, because the force of contraction is surface tension, which decreases on increase in the proportion of soap. Leidenfrost³² assumed as a consequence, therefore, that the force of rupture originates in water and the force of contraction in soap, so that the resistance of the bubbles varies with the concentration of the soap. Gibbs¹⁶ pointed out that the retardation of the process by which films grow thinner cannot be accounted for by the formation of black spots, but may be attributed to a passive resistance to the motion due to the very viscous or gelatinous condition of the film. Also, it is unlikely that the formation of a stable film would occur without the support of such a resistance when rendered unstable during the same process by the precipitation of its mass. On the other hand, gelatinous properties are marked in soap solutions containing more soap than is required for the formation of films. This is true to a remarkable degree in saponin solutions. In an ordinary soap solution, however, no superficial viscosity greater than that of pure water was found.⁴⁴ The resistance to an internal current is not measured by the resistance to motion, and it is doubtful whether a retardation of the tendency toward an internal current between elements adjacent to a black spot, changing slightly in thickness with time, may prevent rupture of the film.¹⁶ In a thick film the increase in surface tension with expansion necessary for the stability of the film is due to the presence of an excess of soap, or its components, at the surface as compared with the interior of the film.

Conclusions

(1) A film undergoes continuous decrease in thickness before collapsing. The thinning effect is produced by the weight of the lamina, as well as by the difference in the pressure at the terminal edge of the film and its interior.

(2) Evaporation and condensation processes influence the transition to the unstable state, depending on the volatility of the components decreasing surface tension. Rupture is facilitated by volatility.

(3) Decrease in the thickness of a film is accelerated or retarded, depending on whether the film is in a dry or a moist atmosphere.

(4) An increase in temperature, which diminishes cohesion and capillary pressure, assists in the collapse of foam under a smaller weight.

(5) The superficial viscosity of a film must be sufficiently high to make thinning of the film slow.

(6) The surface tension should be relatively weak, so as not to overcome the opposing resistance of viscosity.

(7) The ratio between superficial viscosity and surface tension is Plateau's criterion for the unstable state. When the ratio is larger and not proportional to viscosity, foam bubbles collapse.

(8) Two forces act in a bubble—centripetal and centrifugal—the latter being located in the colored portion of the film and concentrated in the “black spot.”

(9) The intensity of rupture of a bubble depends on the concentration of soap.

Foam Prevention

Factors Influencing Foam Prevention

In many industries foaming of liquids may or may not be desirable. As a matter of fact, in the heat treatment of certain liquids, such as emulsified oils, foaming is a highly undesirable effect, and a number of methods are in use to prevent its taking place. In systems which foam, the general method for breaking or preventing the formation of foam is to have a superheating system above the evaporating surface of the liquid.

Pressure and high temperature reduce the tendency of liquid systems to foam. The lack of vapor space prevents substantial foam formation, as found in dehydrating emulsified crude oils.⁵ The properties of emulsified crude oils with respect to foaming are not additive. Intensity and persistency in foaming of emulsified oils to be dehydrated is decided by the nature of the oil. Foaming and the evaporation of water from the emulsified oil are markedly influenced by certain substances, such as gasoline. The foaming of emulsified oil increases as a function of the depth of the oil in the container, reaching its maximum at a definite temperature. Superheating and foaming occurring in the dehydration of emulsified oils give evidence of the existence of a self-cooling effect.

Foaming of liquids often occurs during vacuum distillation. Jetting heated oil aids particularly in the dehydration of foaming oils.⁴⁵ Small jets of emulsified oil are forced against a heated body beneath the surface of the liquid. Foam may be broken by passing it through a series of heated double grating plates.²⁸ When passing the liquid to be distilled over a series of vertical plates, a countercurrent of the vapor prevents foaming.⁶⁰ Foaming during steam distillation may be prevented by the addition of substances acting as defoamers. In most cases substances used in practice prevent or diminish foaming in a particular operation and are not universally applicable. The addition of many organic compounds to a foam made with a glue solution showed that in general fatty acids had a greater effect upon the destruction of foam than the corresponding alcohols.³⁸ No relation was found between the surface tension of the liquid and its ability to destroy foam, but in a homologous series the preventive effect appeared to increase with the molecular weight of the compound. With an increase in the concentration of the glue, the foaming power passed through a maximum. Certain mixtures were recommended for the prevention of foam; a mixture of linseed oil and alkali proved very effective. Petroleum, fat, milk, peanut oil, whale oil, oil of cloves, and various vegetable oils were found to decrease foaming in practice. Removal of sludge has been very often proposed to inhibit foaming. The addition of lime to maintain the pH above the neutral

Table 6. Examples of Undesirable Foaming

Processes	Foaming Agents	Foam Preventers	Remarks
Paper production	Proteins Gelatin Dextrin Casein	Petroleum Fat Milk Peanut oil Oil of cloves Vegetable oils Alcohols of the fatty acid series	
Heat dehydration of crude oils	Introduction of steam into an emulsified oil undergoing dehydration, causing foaming	A mixture of linseed oil and alkali acts effectively in the prevention of foams	In the homologous series, the preventive effect increases with the molecular weight of the compound used
Heat dehydration of tars			Foaming in tars may occur when they contain less than 1 per cent of water

fulfill these conditions. Concentration of the capillary-active substance used as a foam agent is of great importance. A parallel decrease in tension and foam formation occurs only at certain concentration values peculiar to each capillary substance used. Foam formation ability decreases parallel with a decrease in surface activity of the component dissolved in water. The decrease in solubility limits the increase in surface activity. The intermediate members of the homologous series show the most suitable relation between solubility and surface activity (considerable solubility and at the same time high surface activity. The influence of solubility itself is well expressed. Increase in solubility increases foam formation ability. Surface tension changes cause adsorption, resulting in a Gibbs interface layer, made up of various kinds of molecules. There is no foam without a heterogeneous interface layer, and homogeneous liquids are unable to produce stable foams. The wholly molecularly dispersed members of a homologous series allow a greater heterogeneity than the partially colloidally dissolved members. Solutions of surface-active substances foam better the more abrupt the concentration drop between the Gibbs layer and the solution.

Spreading is also a factor to be considered in foam formation. The rate of spreading is not parallel with the rate of surface increase in the formation of homogeneous layers, and the foam walls consist of heterogeneous layers.

The stability of foam systems is usually not great and is expressed in seconds of duration, although sometimes it reaches several days. Permanence may be increased under certain conditions. The coalescence of bubbles in a foam may be prevented by the addition of substances increasing the viscosity or imparting a certain elasticity which softens the skins of the interface. Foams may be classified as lyophilic and lyophobic with respect to their relation to electrolytes. Lyophilic foams have

marked properties, such as viscosity and elasticity, and the influence of electrolytes on them is very small. Lyophobic foams are more stable and therefore less sensitive to electrolytes. Diminution of interfacial surface tension is one of the factors contributing to the stability of a foam system. Besides protective colloids, solids prevent coalescence of foam bubbles, maintaining a permanent foam system. The stabilizing action of a solid in foam systems depends upon the degree of dispersion of the solid and its nature, affinity, and concentration. The ability of a solid to wet is of great importance. Those substances less wetted by water adsorb the capillary-active substance from the aqueous solution forming the Gibbs interface layer. A relation exists between wetting ability, adsorption, and flotation.

Changes occurring in the foam system and leading to rupture of the interfacial film or to its gradual thinning induce an unstable condition. Continuous thinning of the interfacial film by internal currents is due to gravity and strong suction at the edges of the film. The effects of the motion of external molecules, evaporation, and condensation are important. Volatility influences the rupture of the superficial molecules of the film, which are readily lost because of lessening of cohesion due to evaporation. A viscosity great enough to slow down the thinning of the film prevents coalescence of bubbles. An increase in the temperature of a foaming liquid diminishes cohesion and also diminishes capillary pressure so that bubbles collapse under a smaller weight. The relation between superficial viscosity and surface tension should be large enough to make the rupture of the film difficult. The film is subjected to two different actions: (1) weight, which has a tendency to make it thinner, and (2) adsorption which, on the contrary, tends to make it thicker. Where two forces counterbalance, an equilibrium of the foam is reached. Foam systems present a typical case of a dynamic and not a static equilibrium. In the case of a solid used as a stabilizer, the dynamic equilibrium established between the rate of formation of the adsorbed layers of the foam-forming agent, or stabilizer, at the solid/liquid boundary on the one hand, and the rate of such layer formation at the gas/liquid interface on the other hand, determines to a certain extent the stability of a three-phase foam system. Small solid particles may contribute to the stabilization of a froth or foam, as in the case of mineralized froth, or in the ore flotation process, by preferential aggregation in the interface between two phases. Gas bubbles adhere to the solid particles in spite of the electrostatic repulsion of the components. The attraction between components of a foam system should be ascribed to more powerful capillary forces rather than to electrostatic forces. The function of capillary force is to separate the intermediate parts between two bubbles and to prevent coalescence where diminution of the surface occurs.

The adsorption layer in the interface evidently plays a most significant part in the stabilization of foam systems. In calculating the thickness of this layer, Bartsch proved that the maximum stability of these systems corresponds to a monomolecular film. An attempt has been made to

explain the relation between the thickness of the interfacial layer and the stability of a foam system, based on the Langmuir-Harkins theory of the fine structure of the boundary layers for those concentrations of foam-forming agents or stabilizers which lead to permanent foam systems. The intensity of adhesion between solid particles and gas bubbles is caused by the saturation of groups of molecules of the stabilizer rich in residual valences. These residual valences originate in the boundaries of the solid phase and are the result of the influence of the most saturated group of molecules of these substances, decreasing the surface tension at the gas/liquid boundaries, and the free boundary energy acquiring the smallest possible value. For low concentrations, the intensity of adhesion between solid particles and gas bubbles decreases with a decrease in the number of molecules of the foam agent or stabilizer causing adhesion.

At concentrations exceeding the condition of permanence, the adhesion between solid particles and gas bubbles occurs only when the dynamic equilibrium permits the formation of gas/liquid boundaries partially free from adsorbed molecules of the foam-forming agent or stabilizer.

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Chapter 2

Practical Knowledge of Emulsions

EMULSIFICATION

Introduction

Emulsification is restricted to certain limits conditioned by a definite interrelationship between variables for every type of emulsion. This indicates that the history of every emulsion should be described and that only those emulsions should be compared which originate under definite and identical conditions, keeping in mind the following: (1) the emulsifying tendency of the oil; (2) the rate at which an emulsion will develop when agitated; (3) the mechanical treatment of the oil in the presence of the phase in which it is to be dispersed (shaking, mixing, stirring), as well as other means of forming an emulsion; (4) the components of the system added to or present in the system to be emulsified; and (5) the physical conditions under which emulsification processes take place.

There are many methods for producing emulsions, the emulsification method depending upon the nature and the properties of the components making up the system and their relationship. It is evident that emulsification, even of the same components under various conditions, will result in emulsions of different properties, and that the stability will be influenced more than any other property. The controlling factors in the process of emulsification to a stable state are: temperature, mechanical agitation, time, concentration-relation of the emulsifying components, homogenization, presence or absence of foreign substances, degree of dispersion of the internal phase, and changes in the dynamic equilibrium. All these factors not only affect the stability of emulsions, but influence their actual formation as well. Finally, the type of an emulsion system formed has been considered as a function of the conditions under which the system originated. It has been claimed¹⁸ that only one type of emulsion, either water-in-oil or oil-in-water, is possible with a given combination of oil and water, irrespective of the conditions under which emulsification takes place. Today it is generally recognized that the type of emulsion formed is totally unrelated to the conditions under which emulsification takes place and depends chiefly upon the kinds and concentrations of emulsifying agents present.

Roberts,³⁷⁴ studying dynamic dispersion and emulsification under conditions of uniform mixing and continuous agitation, arrived at the following conclusions regarding the factors which determine the type of dispersion: the relative volumes of oil and water used are the controlling factor; the relative specific gravities, viscosities and dielectric constants

of oil and water, the pH of water, and the effects of the emulsifying agent are important factors; the shape and size of the container, the total volume of liquids used, preferential wettability of the container walls, surface-tension differential and interfacial-tension differential are rather negligible factors.

In discussing the processes of emulsification of hydrocarbons in crude oil, distinctions must be drawn between emulsions formed by flowing or pumping from the earth strata, those obtained by various treatments of petroleum, and those prepared in plants and laboratories for practical application. To understand the processes of petroleum emulsification, the main steps in obtaining petroleum, as well as the behavior of the oil (under pressure), both in the interior of the earth and on the surface during and after pumping, must be considered, as these factors determine the emulsification possibilities of the oil.

In the oil field an emulsion (also called cut oil), is composed of two liquids, water and oil, and the emulsifying agent. The emulsifying agent may be one or more of various substances, the most common of which are microscopic paraffin flakes, asphalt particles, clay or earthy matter, certain heavy hydrocarbons, or naphthenic acids and their salts. It is only after agitation of the liquids and the emulsifying agent that an emulsion is formed. The agitation necessary to form crude-oil emulsions is produced by gas bubbling vigorously through the crude oil and water or by the two liquids when forced through relatively small openings at high velocities. Notable cases of gas agitation are naturally flowing wells, gas-lift wells and pumping wells which "pump off." It is known that the place in which emulsions form may vary. They may be formed as the oil and water flow through the oil-sand layer; as they flow, are pumped or gas-lifted to the earth's surface; or as they flow to storage. It is not only reasonable to assume that the formation of petroleum emulsions may be due to water issuing from the earth layers above the oil strata through which the oil passes but, as a matter of fact, it is "bottom water" that causes most emulsion trouble, as it is very difficult to cement off. By sealing this water layer before pumping, the formation of an emulsion of this type may be prevented. In order to form emulsions, the oil and water coming from the oil level in the earth must be subjected to some kind of agitation, for the pores of sands in which petroleum is deposited, or through which it passes together with water, form a system or a series of contracting and expanding channels. Depending upon the degree of graining of the sand, the number of pores and the diameter of these channels change. However, the motion of oil through capillary pores in the sand should hardly cause emulsification, since such flow is usually streamlined because of the small sizes of the pores. The motion of the oil and water within them during migration, as a sequence of the action of pumps, causes squeezing of the petroleum. The pumps and compressors bring the petroleum and water particles into mutual agitation. The space relation of the channels between the sand grains is important in dispersing petroleum and water particles. Another important factor is

the influence of the gas dissolved in the petroleum. This gas in petroleum tends to escape from it and causes an agitation of the oil and water.

Ralph³⁶² emphasizes that little attention is given to the elimination of controllable factors responsible for the formation of emulsions. He states that each pumper or switcher should have a centrifuge machine available and know when and to what extent a certain well is emulsifying its oil. In this manner it would be possible to make recommendations as to the time when well equipments should be reconditioned. Roberts reports that this practice was introduced by the Tretolite Co. in 1924 and was in general use by Phillips Petroleum Co. at Smackover and other places.

Both petroleum and water are subjected to the action of a series of pressures, such as the pressure of the expanding gas, static pressure, forces of gravity, and hydrostatic pressure at the edge of the water, as well as the negative pressure originating under the influence of suction forces produced by the pump. As a result of these pressures, the petroleum stream is pulverized. The nature of drop formation is the reason for emulsion formation. Gurwitsch,¹⁵² discussing the mechanism of drop formation, states that the size of drops in an emulsion is dependent on the diameter of the hole, as well as on other factors; but the smaller the hole, the smaller the diameter of the drop. The pores of the sand are small capillaries. Wischetravsky⁴³⁵ pointed out that when a liquid is forced through a narrow tube, the stream is compressed and an inrush of air takes place at the interface, *i.e.*, between the stream and the tube, which is a classical example in hydraulics. The action of the gas in the stream, according to Uren, is comparable to that of an injector. The oil passing through narrow holes forms an elongated drop and then breaks off, acquiring the usual round shape. Photographs in Suman's book illustrate this process of drop formation in an oil emulsion.

Nutting,³³⁰ discussing the formation of oil-field emulsions, describes what happens when merely muddy water is shaken with gasoline. The oil and water separate clearly, leaving the solid ingredients in the form of a thin skin at the interface and on the glass wall. The skin formed by the fine particles is tough and may be lifted out on a wire like a piece of wet rag. On drying, it returns to a powder, indicating that no permanent chemical change has taken place. The solid particles adsorb the two liquids and mesh together.

Wischetravsky⁴³⁵ considers the factors repressing the action of surface tension as making possible the mixing of petroleum and water. The force which tends to decrease the interfacial area is greater when the petroleum drop is exposed to air than when it is touched by water, indicating that the force pulling the petroleum drops together at the water/oil interface is less active. The same holds true for the surface tension of water drops at the water/petroleum boundary, causing a reciprocal weakening of the surface-tension forces and the establishment of an equilibrium between the water and oil particles. That this is actually the case Wischetravsky illustrates in a figure in which he shows that the

boundary between petroleum and water is not horizontal, but is peculiar in shape, being subjected more to the influence of the shape of the container than is in accordance with the laws of tension. The dispersion or drop formation occurring by dropping into the surrounding medium assists in mixing the components and brings about the emulsion system. In a gas-lift well, the rapid expansion of the gas produces shearing forces and the turbulent motion mixes the water with the oil drops. This results in a rather thick mixture of petroleum and water and may even form a homogeneous mass. Thus emulsification in wells may be localized within the oil sand or may occur at any point in the well or pumping equipment where there is turbulence of fluid flow.

The conditions attending the production of oil in either free-flowing, gas-lift, or pumping wells are also conducive to emulsification. That the formation of emulsions in the oil sand increases with the rate of flow and is aided by the presence of gas bubbles is mostly the case in the immediate vicinity of the wells; back in the sands the flow velocities are too small to produce appreciable emulsification. The quantity of emulsion formed may be diminished by reducing the flow of the fluid components; whether quasi- or true emulsions are formed depends on the intensity of agitation. Quasi-emulsions, when filtered, show a complete separation of oil and water, whereas true emulsions are difficult to filter under ordinary pressure. The difference between a true emulsion and a quasi-emulsion depends solely upon the character and stability of the emulsion film at the interface. If the globules are above a certain diameter, they sometimes can be separated from the oil by mechanical means or by forces, such as gravity. In other cases, for example, gas-tar emulsions, even extremely coarse division results in a very stable state; likewise tank-bottom emulsions and some freshly produced emulsions in low-gravity oils attest the great stability of coarsely divided systems. If the globules are small, the separation of water is not effected by any mechanical force; temperature, or temperature and pressure, as well as chemical, physico-chemical, or electrical means are useful. The change in the velocity of the flow is technically accomplished by using a back pressure on the well or by increasing the diameter of the well.³¹⁶ On the other hand, the rate of flow through the well is proportional to the surface area of oil sand exposed. Thus every device or method used in lifting oil from the wells causes agitation in the oil and water produced. High velocities are present because of large volumes of gas, present in many wells, which are forced through tubing, pipe bends, valves and control devices of small cross-section, which add to the agitation of the oil, water and gas to produce emulsions. In addition to flowing wells and gas-lift wells, conditions favorable for the mixing of oil, gas and water are met with in cases of slippage of gas through the liquid, combined with variable flow velocities in different parts of the pipe. Among all devices, the most potent cause of emulsification is pump valves. Emulsification can be reduced to a certain extent when the pumping speed is regulated and tight valves are used. Care should be taken in removing gas and water from

the oil before the oil is forced through flow lines. In swabbing wells, considerable emulsification of water and oil may occur. Lowering of the swab into and through the well fluid should be done slowly, a proper clearance between tubing and swab being maintained at all times. It must be mentioned also that incrustated or corroded pipe walls cause turbulence in the fluids.

The tendency of oil and water to emulsify in wells flowing under high pressure is increased by the forced passage of the mixture through a restricted opening in the choke nipple or flow bean placed in the flow line to maintain back pressure on the well. Most emulsification occurs on the downstream side of the choke, where violent turbulence takes place because of the rapid expansion of the gas. Miller^{311a} stated that the percentage of emulsions at many gas-lift wells has been reduced by eliminating the flow nipples in the eductor line and by holding the desired back pressure in the gas separator instead of using flow beans at the well head. In the Oklahoma and West Texas fields the reduction of emulsification in naturally flowing wells is accomplished by using bottom-hole chokes.

Emulsification resulting from the increased velocity of the expanding mixture passing through the constricted passages of the pump valves and cages may be eliminated by excluding as much gas as possible from the pump. A gas anchor, which prevents gas associated with oil and gas evolved from solution in the oil from entering the pump barrel and causing agitation and heading, has been described by Robinson.^{375a} Fig. 1 shows this gas anchor. Oil and gas enter the anchor and start to flow downward in the space between the outer pipe and the inner tube, called "mosquito bill." The velocity must be less than the rate of rise of the gas bubble through oil (the rate of rise is normally above 6 inches per second in water). The capacity of an anchor is proportional to the down-pass area. Anchors are about 21 feet long. Gas anchors are placed at a point in the well where the oil inlet to the anchor is not submerged below the normal working-fluid level. Low pressure must be maintained in the casing. The use of gas anchors is limited to wells in which fluid levels are maintained constant and little or no back pressure is held on the sand by maintaining pressure at the casinghead.

In general, emulsification is more pronounced in deep wells than in shallow ones because of the greater static pressure on the top plunger area, which causes the fluid to jet past leaky plungers in valves at high velocity. Under high static pressures in deep wells some slippage is inevitable, and this favors the formation of emulsions. Methods of combating slippage have been given by Schnobrich.^{384a}

The submergence of a pump is an important factor. If it is sufficient so that the wells do pump off (fluid is removed at a faster rate than it enters the hole), pumping of the wells after they begin to "pump off" (air or gas is drawn into the pump) reduces volumetric efficiency and sets up a churning action causing emulsification of oil and water with each stroke of the plunger. A reduction in the hours of pumping, the use of a

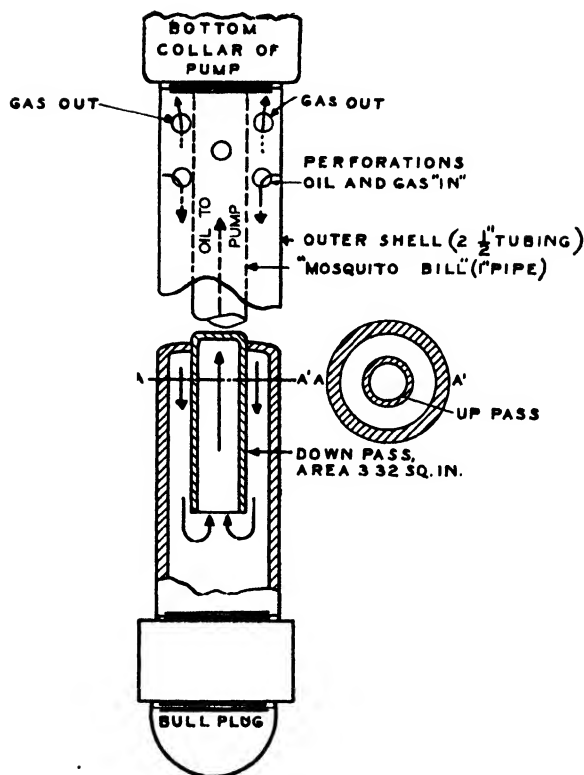


FIG. 1. Gas anchor (oil and gas separator); theoretical capacity, with effective oil velocity of 6 inches per second, 178 barrels per day. (After Robinson, B. H., "Economics of Pumping, Drilling and Production Practice," American Petroleum Institute, 1935.)

smaller pump, and pumping at a slower rate are suggested measures for avoiding overpumping.

To reduce turbulence and emulsification, as well as gas action in the plunger, close spacing between the plunger and the standing valve in the pump has been recommended. Spacing of plungers to provide minimum clearance volume is especially important in deep wells. Leakage past pump valves is an even more common source of emulsification than slippage past plungers. A worn or a leaky pump valve results in the appearance of an emulsion in a well. Pump valves are subjected to severe pounding at each stroke, as well as a chattering action of the ball against the seat. Leak in the tubing in a well producing oil and water sometimes causes emulsification. The fluid pressure within the tubing forces the fluids through the opening into the annular space between the tubing and casing, and this causes emulsions to form. Therefore, maintaining pumping equipment in the best condition is an important part of oil-well operation.^{389a}

Paraffin accumulation in wells and flow lines acts as a choke by restricting the flow, increasing flowing pressures and turbulence, and thus constituting a source of emulsification. Reistle^{387a} discusses causes and methods for preventing accumulation of paraffin in wells and flow lines.

The tendency to emulsify is influenced by the percentage of water in the oil. A large percentage of water often does not emulsify as thoroughly and permanently as a small amount. It is known that additional water circulating continuously lessens or prevents the formation of emulsions; a circulating pump is used for this purpose. Salt water is preferable to fresh water because of its higher surface tension. The type of emulsion formed depends upon the predominant emulsifier in the crude petroleum. If the crude oil contains a hydrophobic colloid, and if either fresh or salt water is gently agitated with it, there is a tendency to form an emulsion in which the water is suspended in the crude oil. Soap is an example of a hydrophilic colloid; thus soap solutions tend to form an emulsion in which the oil is the disperse phase in the soap-water. If the hydrophilic soap is present in a relatively large proportion, it exerts a stronger action than the hydrophobic colloid of the crude petroleum, and this results in an emulsion with water as the continuous phase. The ability to emulsify in most mineral oils is so great that Rakusin³⁸¹ terms them "hygroscopic bodies."

Natural and artificially prepared emulsions are known, depending upon their origin. Artificial emulsions are found where oil comes into contact with wet steam; this occurs by alkalization during the refining of oils, or when lubricating oils form emulsions in steam engines. The refining process of mineral oils consists essentially of two parts: (1) treatment with acids, and (2) treatment with alkalis. In the second case, the oil becomes intimately mixed with sodium hydroxide, often resulting in very stiff emulsions. In the case of lubricants, water present in the form of very small droplets favors emulsification and the motion of the engine produces an intimate mixing.

In a great many cases emulsions form readily but are undesirable; there are also cases in which their formation is desired, but it is very difficult to form them. The term "water-soluble oils" is incorrect because it is very seldom that they actually form clear solutions with water; instead, very fine emulsions are formed. These emulsions are used as cheap lubricants for workshop engines, cutting oils for tools, etc. Water-soluble oils are prepared by dissolving alkali or ammonia soaps in mineral oils and intimately mixing with water to obtain a very fine division. Especially good results are obtained when acid soaps are dissolved in mineral oils.

In all cases of emulsification, the ability to emulsify depends greatly upon conditions under which the emulsion formation occurs. Factors influencing emulsification, such as the nature of the components, their specific gravities, temperatures at which emulsions are formed, mode of agitation, time factor in agitation, the particular process chosen for the

production of an emulsion, the addition of agents aiding emulsification, etc., are subjects for discussion. A difference in the specific gravities of the emulsion components, in general, should not favor emulsion formation; as a matter of fact, equal specific gravities are best, because no settling effects could aid in resolving the dispersion. Viscous liquids emulsify, in general, more readily than less viscous, although the behavior of an emulsion system with respect to various factors is quite individual. The cause for the marked difference in the behavior of emulsified oil during emulsification under heat treatment is not definitely known. Pickering,³⁵¹ in his "Note on Emulsions," states that almost all emulsions with which he experimented were prepared in the cold, and that in comparing these emulsions with "similar" emulsions prepared at higher temperatures, the results obtained were identical. Further, he states that high temperatures greatly facilitate emulsification; and in extreme cases where a mixture does not emulsify in the cold, it may be emulsified by application of heat. Pickering's conclusions are based on an investigation of paraffin soap solution systems. Some emulsions, when heated to their boiling point, did undergo a sudden change, separating into water and oil, while no apparent change in the appearance of the emulsion was noticed when the temperature was reduced several degrees below the boiling point; however, as soon as the boiling point was reached, the water separated out rapidly. On the other hand, there are emulsions which, when heated to 221° F and held at that temperature until all the water and part of the oil have been distilled over, at no time show any disintegration. It may be that the difference in the behavior is due to the gravity of the oil from which the emulsion is formed, or it may be due to the amount of foreign material present acting in a protective capacity. Experiments carried out by different investigators proved that in the case of insoluble emulsifiers neither an increase in heat nor an increase in volatility favored emulsification; indeed, an increase in volatility retarded it, perhaps because the more volatile oils are also more mobile.

Oil globules in an emulsion are subject to Brownian movement, provided the system is stable. Brownian movement helps to keep the oil globules in a state of suspension, the movement being due to the bombardment of oil particles by the molecules of the continuous phase, and is a series of uncoordinated collisions. The oil particles execute a zig-zag motion the intensity of which is inversely proportional to the radius of the particles dispersed and to the square root of the time (the diffusion constant = the distance the particles move). An increase in temperature on the one hand causes an increase in Brownian movement and a higher frequency of collision of the dispersed globules; on the other hand, evaporation of the continuous phase retards Brownian movement and sometimes stops it altogether. The relationship between these two factors directs the influence of the temperature. Heat influences the emulsion system to be formed by displacing the state of equilibrium in the system. In the case of foreign substances and emulsifiers, this may be of great importance. The choice of conditions under which an emulsion is pro-

duced must be made within reasonable limits. Agitation under certain conditions may cause the formation of an emulsion system, but under other conditions it may cause its break-down.

Methods of Preparing Emulsions

Emulsions are formed by shaking, intermittently and uninterruptedly, using stirring arrangements, rolling or dragging, or rotating in cylindrical bottles containing the components of the future emulsion, employing special devices for dispersing, such as colloid mills and homogenizers, mixing by means of flowing gas, high-velocity nozzles, or centrifugal arrangements, etc. Pickering³⁶¹ recommends the use of a garden syringe fitted with a rose nozzle as the simplest expedient for emulsifying the components of an emulsion, as it is apparent that this type of nozzle splits the hydrocarbon phase into very minute particles. When paraffin is used in such a device, it appears to rise from the liquid in the form of mist, a one-minute period sufficing to emulsify. A continuation of the operation for three or four minutes does not modify the result previously obtained. According to Pickering, if a mixture does not emulsify immediately, no further pumping can force it to do so.

Briggs⁴⁶ effected complete emulsification of 90 volumes of benzene in 100 volumes of mixture in two minutes of continuous rolling. According to Clayton,⁷⁷ continuous shaking would give just as good results as intermittent shaking, provided that the emulsified portions of the mixture are continually removed from the mass so that the energy of shaking is concentrated on the portion remaining. If this is correct, then where the disperse phase is injected into the external phase below the surface, intermittent injection would have no advantage over continuous injection, as stated by Clayton. On the other hand, the formation of a complete emulsion is facilitated by allowing the emulsion complex and the discontinuous phase to form two distinct layers before each shake. This would indicate that emulsions are formed most readily when relatively little oil is agitated for a short period of time when in contact with a relatively large and unbroken volume in which the soap solution is the continuous phase. Continuous shaking in a bottle disintegrates both the disperse and the continuous phase with the formation of drops; but since the soap-water solution is the continuous phase in an emulsion, any process tending to disintegrate it must retard emulsification; likewise, a process tending to disintegrate the phase to be dispersed aids emulsification. Therefore rapid and easy emulsification should be anticipated whenever the phase to be dispersed breaks up into drops under conditions unfavorable to the simultaneous disintegration of the continuous phase or with least disintegration. The time and the number of shakes required to complete emulsion formation vary with the rest interval between shakes. In shaking emulsions direct, intermittent shaking is far more efficient than uninterrupted shaking, even in a shaking machine. Agitation produced by stirring requires knowing the number of revolutions per minute of the

agitator in order that it be not too high and identical for consecutive emulsification tests.

Roberts,³⁷⁴ comparing continuous and intermittent (single-stroke) agitation, found that the latter is approximately twenty times as efficient as the former in producing a stable water-in-oil emulsion. Whereas continuous agitation with percentages of water above the lower limit for the formation of an oil-in-water dispersion hinders the formation of a water-in-oil emulsion by maintaining the dispersion of the oil in small droplets, intermittent agitation facilitates emulsification by furnishing opportunity for coalescence of droplets during the rest periods, and prevents formation of exceedingly fine dispersions of oil in water.

The experiments of Freundlich and Kroch¹³³ established the fact of mechanical coagulation of colloids; and, of course, the same holds true for emulsions in which the lack of control of factors producing mechanical agitation may lead to resolution instead of the formation of an emulsion system. It is, therefore, reasonable to believe that for any emulsifying apparatus or machine an optimum speed or degree of agitation or mixing, as well as an optimum time of operation, must be determined, whereby a stable emulsion is obtained for a given system. In some cases even the type of emulsion may be dependent upon the mode of shaking. It has been observed that gentle shaking favors the oil-in-water type, and that vigorous shaking favors the water-in-oil type. Woodman⁴³⁸ claimed this is the case for cresylic acid-gelatin-water systems. Clayton considers that this is by no means generally true. He⁴³⁹ states that, by shaking the water and the non-aqueous phase in various ways, many types of emulsions are formed, the different mechanical conditions apparently influencing the distribution coefficient of the emulsifier in the two phases. Wilson⁴³⁴ found that by emulsifying benzene in water, with sodium oleate as emulsifier, gentle continuous shaking resulted in the formation of the water-in-oil type, whereas vigorous intermittent shaking gave oil-in-water emulsions. The emulsions could be reversed on homogenization if enough oleic acid was present. Likewise, if benzene was added to water in 5-cc portions, with shaking after each addition, the emulsion formed was of the oil-in-water type. On homogenization, it could be reversed.

Rolling the oil layer over soap-water also serves to agitate an emulsion system. One way of doing this experimentally is to employ a mortar and pestle, as is done in the so-called continental method. Rolling a mixture of oil and soap solution in a cylindrical bottle is another method, the rolling occurring backward and forward. The total distance traveled by the rolling bottle, and the time required for complete emulsification should be recorded. Colloid mills undoubtedly lead to a much finer degree of dispersion of emulsions, but they are objected to on the ground that they incorporate air in the emulsions. Also, with very concentrated emulsions, difficulty is often encountered because of instability of the emulsion system.

Clayton⁷⁷ proposed carrying out emulsification and homogenization of the emulsion system simultaneously in one machine. A homogenizer

should be so constructed that it operates on the principle of injecting the internal phase into the external phase, the injection and atomization being of such a character that an already homogenized emulsion would immediately follow. Clayton also questions the influence of vapor pressure on the disperse phase. In emulsification by condensation of a vapor in a liquid, a progressive decrease in the mean radius of the globule occurs with an increase in pressure. This is caused chiefly by the more uniform dispersion produced by the increase of vapor pressure.

Sumner^{329, 376} found that the uniformity of dispersion is largely dependent on an efficient distribution of the vapor throughout the aqueous phase during the condensation process, the latter depending on the linear velocity of the issuing vapor.

Mixing liquids by means of gas flowing through them¹⁵⁹ is considered in some quarters to be unsound practice, since the adsorption is pronounced in a resisting froth instead of a liquid/liquid interface. For water contents as low as 25 per cent, better results are obtained by agitation with a saturated salt solution. For a lower water content, it is possible to obtain a more thorough emulsification of saturated salt solution with a soap-water emulsion than can be ordinarily obtained with a stirring arrangement by using a high-velocity nozzle or a centrifugal arrangement.

Briggs and Schmidt⁴⁸ used a shaking machine which produced a lateral motion approximating 400 oscillations per minute. These same investigators endeavored also to determine the time required to emulsify completely mixtures containing different proportions of benzene and one per cent of sodium oleate. The combined volume of benzene and aqueous solution was kept constant at 50 cc. Curves which Briggs and Schmidt obtained represent the relationship between time for complete emulsification (plotted on the abscissa) and the percentage of benzene (plotted on the ordinate), and show that the necessary amount of shaking increases with the percentage of benzene to be emulsified, at first slowly and then with rapidly increasing speed, until the amount of shaking becomes infinitely great. On the other hand, the curve is displaced not only with the change in size and shape of the bottle used in the shaking machine, but with the speed and the mode of agitation, and is changed to a certain extent with the strength of the emulsifier applied. Sheppard³⁹⁰ found that nitrobenzene may be emulsified in sulfuric acid by gentle and rapid shaking, or slow shaking; in certain cases, a single vibration results in demulsification. The method of emulsification is individual. Continuous shaking may disintegrate both phases of the emulsion. Vibrations involved in the shipment of emulsions by truck or railroad also contribute to the breakdown of emulsions.

Ayres¹⁶ quotes a case of an oil-field emulsion so stable as to resist separation in a centrifuge, but which was separated into its components after transit in an express train. Newman³²³ states that the character of the emulsions which he obtained varied markedly with the degree of shaking. Harkins and Beeman¹⁵⁴ confirm this statement by saying that

the method of mixing affects the distribution of the disperse phase. Emulsions produced by a high-speed drink mixer were compared with those made by a motor-driven egg-beater. The size of the largest drops was found to be less for the former than for the latter. Also, the number of large drops decreased with time of stirring, rapidly at first and more slowly later. Ayres indicates that excessive agitation increases the size of the emulsion globules. The hand shaking method is, of course, very

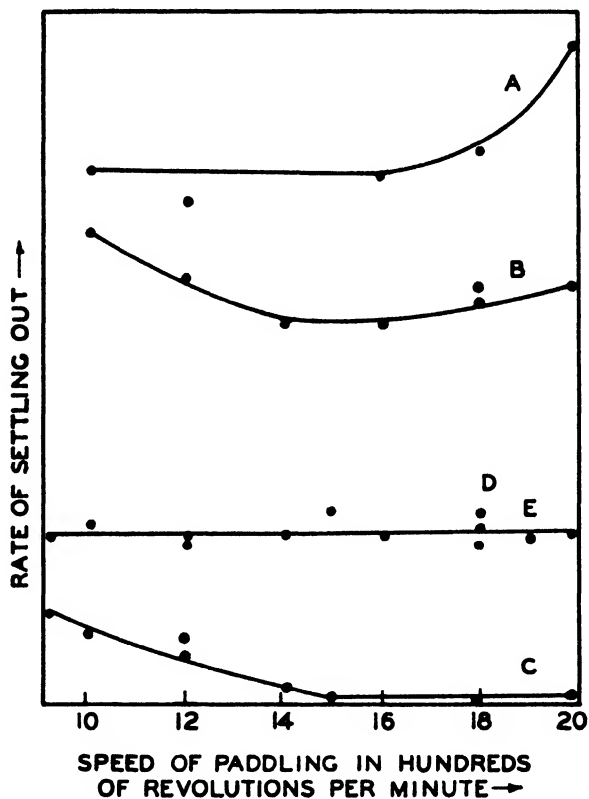


FIG. 2.

primitive, operating in some cases satisfactorily and in others poorly. Herschel¹⁰² found that increasing the speed of paddling produces an increase in emulsification up to 1500 revolutions per minute, above which speed the emulsification decreases with certain oils (Fig. 2). Agitation over too long a period of time also is inadvisable, as shown by Moore's experiments.³¹⁴ Fig. 3 shows the influence of time, at constant speed of paddling, upon the efficiency of emulsification in the case of a water-oil emulsion with lampblack as the emulsifier.

Specific effects on emulsification were claimed by Ostwald,³⁴³ Hoffman,¹⁶⁵ and Briggs and Schmidt,⁴⁸ who found that a different type of

emulsion is formed, depending upon whether the glass surface of the container in which the emulsion has been prepared is wetted with oil or water. The liquid wetting the walls tends to become the outside phase, this tendency being small when the relative volumes of the components forming an emulsion increase. This is definitely not valid, as can be readily determined by experiment. The nature of the emulsifying agent determines the character of the emulsion.

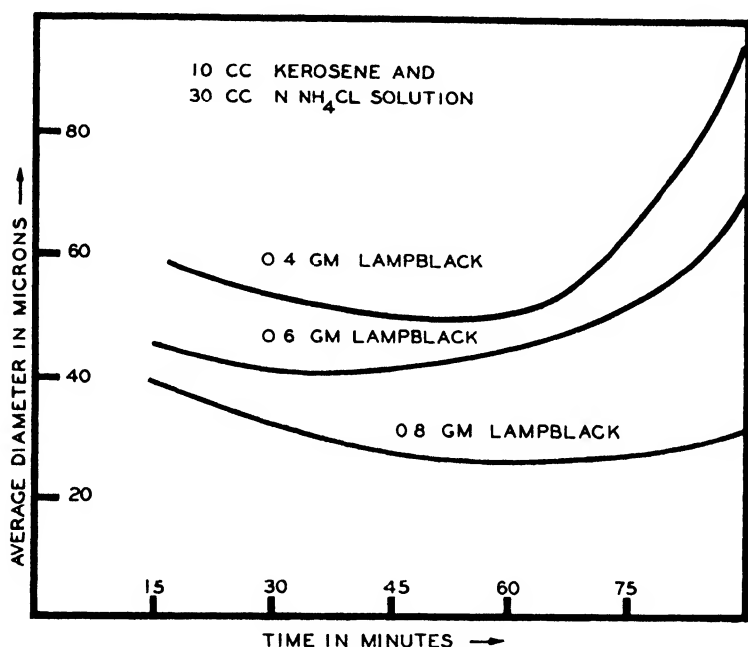


FIG. 3. Effect of Time at Constant Speed of Paddling on Efficiency of Emulsification.

Ssychra and Ssegal⁴⁰⁰ pointed out various factors influencing the degree of emulsification for various soaps. Castor-oil soap shows the highest degree of emulsification at ordinary temperature. Cottonseed-oil soap has a higher degree of emulsification than the so-called "olein soap" from oleic acid. Resin soaps have a higher degree of emulsification than fatty acid soaps. Electrolytes, such as 0.25-1.0 per cent of alkali, increase considerably the emulsification of oleic-acid soaps, ricinoleic-acid soaps and resin soaps at ordinary temperature. The emulsification of resin soaps is greatly increased by the addition of 2 per cent of sodium chloride and more so by one per cent of sodium hydroxide. The composition and viscosity of the substances to be emulsified influence the degree of emulsification.

Speakman and Chamberlain³⁹⁹ considered the degree of emulsification to be determined not only by the magnitude of the interfacial tension and the formation of a stable adsorption film, but also by the length of the

carbon chain. Seifriz's³⁸⁹ findings prove a relationship between the stability of an emulsion and the density of hydrocarbons. Snell's experiments³⁹³ indicate that in mixtures of soap and alkali salts, sodium oleate has the highest emulsifying value of the substances investigated, and that sodium silicate, sodium phosphate and dibasic sodium phosphate are not efficient emulsifiers on account of too low a hydroxyl concentration.

Kremnev,²⁸⁷ studying the emulsification of mercury in benzene, with oleic acid as stabilizer, which resulted in the formation of a mercury foam of poor stability due to low viscosity and high gravity, found that hemispherical air bubbles enclosed by a mercury shell are important in the emulsification process. In a benzene-sodium oleate solution the bubbles break at the air/benzene interface, and the drops collapse because sodium oleate does not stabilize water-in-oil emulsions.

Wood and Loomis^{436, 437} and Richards and Loomis^{370, 371} studied the effect on the process of emulsification of ultrasonic waves (100,000-500,000 per second), produced with the aid of a piezoelectric quartz plate between electrodes connected with the poles of a Tesla coil. The first experiments were concerned with the dispersion of mercury in water under the influence of ultrasonic waves. Söllner and Ragowski³⁹⁶ investigated the phenomenon for mercury and water, as well as for liquid pairs, such as water in benzene, in the presence of a gas, which proved to be of great importance in the formation of an emulsion. It was observed that no emulsion is produced *in vacuo*. The effect of oxygen and hydrogen and, in some cases, nitrogen and argon, was ascertained. It is presumed that emulsification may be poor in liquids in which mercury is strongly wettable; for example, mercury is not emulsified in gasoline. Bondy and Söllner^{39, 329} believe that the dispersion of mercury is due to the bursting of bubbles of the other liquid coated with thin films of mercury. Mercury emulsions are stabilized by adsorbed gases.

Freundlich^{131, 132} and Freundlich and Söllner¹³⁴ explain the mechanism of ultrasonic waves in emulsification processes by assuming a direct dispersing action due mainly to transverse vibrations of the walls of a capillary U-tube in which the emulsification takes place. Striations of great regularity are formed in a short time in both branches of the tube (see figure from Clayton, p. 317). The droplets collect in the nodes, while the antinodes remain clear. The distance between two nodes is equal to half a wave-length in the liquid. The striations formed are considered by Freundlich as relating to Kundt's method for determining the wave-length of sound waves. According to Freundlich, ultrasonic waves have no specific properties to which emulsification may be attributed, but they do contribute mechanical energy, similar to devices producing shaking or stirring, only to a greater extent.

Bondy and Söllner^{39, 329} consider cavitation at the interface to be a cause of emulsification, the cavitation being favored by dissolved gases acting as nuclei, while the external hydrostatic pressure exerted by gases is essential to the collapse of these cavities, and high pressure may be unfavorable to emulsification. In a later paper, Bondy and Söllner³⁹

conclude that cavitation is essential for the emulsification of oil in aqueous systems, and that it is of no significance whatsoever in the ultrasonic dispersion of mercury.

The mechanism of formation of mercury emulsions in water by ultrasonic waves, based probably upon the pressing of water into mercury, is different from that of emulsifying oil in water. In mercury emulsions the formation of empty spaces plays no significant part. The presence of gases such as air, nitrogen, oxygen or hydrogen is found to increase greatly the stability of emulsions prepared; in the absence of these gases, the emulsions settle out rapidly and the sediment flows together. The reason for the emulsification of organic liquids in water is based on the formation of empty spaces within the liquid; this may occur, for example, by a decrease in the hydrodynamic pressure upon liquids under vapor pressure.

The foregoing factors have much less effect than the nature and properties of the emulsifying agent in determining the process of emulsification. For this reason special attention should be drawn to the nature of emulsifiers, as well as to the reason for their decided effect on the formation of emulsion systems.

Emulsifiers

Davey,^{80,87} discussing the preparation of emulsions by means of emulsifying agents, points out the following cases: (1) emulsifiers have molecules which are not set free readily at ordinary temperature; (2) emulsifiers have a weak adsorption affinity for the water phase (oleic acid; (3) emulsifiers, such as soaps of polyvalent metals containing a methyl group, surpass in their action those containing carboxyl groups bound to the polyvalent metal; (4) the water-oil ratio is so low that flowing together takes place; and (5) dispersion of the emulsifier by the oil phase, as a result of mechanical treatment, causes spontaneous emulsification. Schindler,³⁸² in his article on the precipitation rule for emulsions on the basis of sulfonated oils, emphasized the fact that the value of a substance as an emulsifying agent depends on the method of producing the emulsion and specifically on the substance to be emulsified.

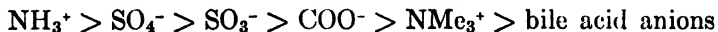
Concerning the nature of emulsifiers, those molecularly soluble or colloidally dispersed in water should be distinguished. When oil-soluble hydrophilic colloids are dissolved in oil, it may be very difficult or even impossible to produce stable emulsions of the water-in-oil type by agitation; and, conversely, when water-soluble hydrophobic colloids are dissolved in water, it may be very difficult to form stable emulsions of the oil-in-water type. If the emulsifier is hydrophilic, like gelatin or gum arabic, the formation of an emulsion dispersed in water is favored. A hydrophobic emulsifier, such as resin soap, favors the formation of an emulsion of the water-in-oil type, generally in organic liquids. On the other hand, powdered emulsifiers, such as lampblack, decidedly hydrophobic, favor the formation of water-in-oil emulsions. Oil-field emulsions are generally classified as the water-in-oil type, assuming them

to be formed, therefore, from colloidal substances dissolved in oil, or from solid substances readily wetted by oil.

Electrolytes soluble in the water phase and either hydrated earth substances or heavy hydrocarbons, such as asphalt, present in the oil as colloids, also act as emulsifiers. It is to be expected that hydrated earths are more readily wetted by water; but there is also a belief, entertained by Sherrick,³⁹¹ that hydrated earthy material may become a hydrophobic colloid by adsorbing heavy asphalt-like bodies of the crude oil, and that this, together with asphalt-saturated earthy material having an unusual wettability, is responsible for the formation of field emulsions. Lottermoser and Calanter³⁹⁰ consider hard asphalt and petroleum tar also to be hydrophobic colloids acting as emulsifiers and producing natural water-in-oil emulsion systems. Both emulsifiers decrease surface tension in the oil/water boundary and accumulate at the interface, forming a protective film. Both emulsifiers increase the viscosity of petroleum, thus favoring the stability of the petroleum emulsions formed. Hard asphalt is thought to produce more stable emulsions than petroleum tar. In accordance with his findings, Dow¹⁰⁵ concluded that asphaltic material, *i.e.*, the high-boiling fractions of petroleum, are most important in the emulsification process.

Schulman and Cockbain^{388a,b} state that with some emulsifying agents emulsification is brought about "spontaneously" by hand-shaking for 2-3 seconds, whereas with other agents special homogenizers must be used to lower the interfacial tension. The interfacial tension in spontaneous emulsification must be extremely small (a fraction of a dyne per cm). Schulman and Cockbain's investigations show also that formation of stable emulsions of the Nujol-in-water type may be the result of using an emulsifier consisting of two substances, one of which is oil-soluble and the other an ionizable water-soluble substance. A stable equi-molecular complex is formed at the Nujol oil/water interface when cetyl sulfate penetrates a film of cholesterol. The degree of interaction between polar groups of the film substance and the penetrating compound is of importance. When cholesterol acetate or stearate is used instead of cholesterol, stable Nujol-in-water emulsions are not formed.

Schulman and Rideal^{388c} found that the reactivity of polar groups toward the alcoholic group of cholesterol may be given by the following series:



Emulsifiers commonly used are soaps, resins, proteins (casein, gelatin, albumin, hemoglobin, gliadin), protein hydrolysis products (peptones, gelatines), water-soluble gums and mucilages (gum arabic, tragacanth, Irish moss), colloidal carbohydrates (starches, dextrans), egg yolk, lanolin, cholesterol, lecithin, saponin, sodium salts of sulfonic acids, sulfonated oils, gum resins (dammar, rosin), amylene and insoluble powders.

Not only the kind of emulsifier but also its emulsifying efficiency is of importance in the production of emulsions. Holmes and Williams¹⁰⁷

investigated the emulsifying efficiency of organic compounds, from which they concluded that alcohols, particularly methyl or ethyl alcohol, can be used to advantage. The emulsified system was benzene in water. Propyl alcohol is inferior and butyl alcohol, poor. In fact, the higher alcohols were found to be useless as emulsifying agents. Glycol, glycerol and sugar had no noticeable effect; allyl alcohol showed a pronounced effect but not equal, however, to that of ethyl alcohol. Phenol and resorcinol showed distinct power to emulsify, but the naphthols did not. Benzyl alcohol does not emulsify at all. Acids, such as stearic, palmitic, oleic and linolenic, were found to vary in their efficiency; but acids below caprylic in the fatty acid series were incapable of emulsifying. The sodium salts of sulfonic acids were far superior to the free acid. In addition, esters, aldehydes, ketones and nitriles were tested.

It is said that neutral fats have a decided tendency to act as emulsifiers. The carboxyl group of an ester, together with a hydrocarbon radical, must be less polar than the carboxyl group of a free fatty acid. The aldehydes are of little importance as emulsifiers, but benzonitrile is comparable to the best polar agents. Nitro and amino compounds, as well as the ketones, were found to have little, if any, effect. The water-soluble salts of the hydroaromatic carboxylic acids, such as the salts of propyl or butyl cyclohexanol carboxylic acid, are excellent emulsifiers. It has been found also that with a heavier molecular nucleus such as, for example, the salt of isopropyl tetrahydronaphthalene carboxylic acid,³⁸⁴ the emulsifying action is improved.

The I. G. Farbenindustrie A.-G.¹⁸⁶ claimed as emulsifying agents salts or free acids of sulfonated, alkylated and aralkylated or arylated aromatic or partially hydrogenated aromatic hydrocarbons, excluding diaryl-ethane obtained from styrene. As examples may serve sulfonated benzyl-butyl naphthalene, phenylbutyl naphthalene (from naphthalene sulfonic acid, chlorbenzene and butyl alcohol), benzylamylbutyl naphthalene, benzylbutyltetralin, benzylcyclohexyl naphthalene and the product of sulfonating a mixture of oleic acid, naphthenic acid and aromatic hydrocarbons.

Bennett²⁹ indicates a new emulsifier, namely, trioxyethylaminostearate and ammonium oleate. The stearate is a soap-like body, soluble in water and in hydrocarbons, and does not decompose on melting. To prepare emulsions with this emulsifier, the product is replaced by wax or a hydrocarbon gel in the oil to be emulsified at 60-70° and stirred continuously with the addition of corresponding amounts of water. The ammonium oleate is a paste and is so treated that it is dissolved in water and the oil added with stirring. The emulsions obtained are suitable as cleaning and polishing materials.

Whatmough⁴³⁰ states in his patent that emulsification takes place in the cold more rapidly without the use of a solvent for the oil when a soap is produced *in situ* at the interface between the oil and water in the presence of a protein. Such a protein acts as a buffer, preventing undue variation in the electrolytic activity of the aqueous phase during emul-

sification (the pH of the water is suitably adjusted), and thus the result of emulsification depends on the proportion of alkali in the aqueous phase. The emulsification process consists in mixing a small percentage of a higher, non-volatile fatty acid with a fatty oil. This mixture in its turn is mixed with water containing a protein in which a small proportion of alkali is present. The latter is the percentage necessary to make the electrolytic activity such that the interfacial tension is sufficiently reduced.

Jones^{270, 271} also obtained emulsifying agents by bringing together aqueous dispersions of animal proteins in water, using a relatively dilute solution of sodium hydroxide at temperatures below 100°. Soaps, protective colloids and stabilizers may also be added. Murphy³¹⁸ treated animal albumin and similar substances with a dilute alkali solution below 100° and mixed this with emulsions of mineral oils, bitumen, or tars. Billingham^{32, 33, 34} recommended a pure protein or a material containing not less than 80 per cent of commercially pure albumin, casein saturated with water, and caustic soda or potash. The latter is taken in an amount of 50 to 100 per cent by weight of the substance and used at a temperature below 60°, so that dissociation of the amido fatty acid is effected without saponification and gives an emulsive reagent which may be applied for emulsifying oils, bitumen, or artificial bitumen materials.

Jones²⁷² emulsified oil with calcium caseinate by adding lignin liquid, dextrin, and water and transformer oil. Free carboxyl and hydroxyl groups are present in the final product. An emulsifying agent for fatty oils and bituminous substances is obtained, according to Barnfield,²⁰ by mixing aqueous dispersions of animal proteins with dilute caustic alkali solutions at a temperature below 100°. Lottermoser and Calanter³⁰⁰ indicate the activity of casein as an emulsifier for petroleum. The concentration of 0.2 per cent of casein suggested by Seifriz is not sufficient for all kinds of oil, *e.g.*, Baku oil. Casein, in general, stabilizes oil-in-water emulsions when oils, as in the case of refined petroleum, do not contain natural emulsifying agents. When the oil does contain such agents, either oil-in-water or water-in-oil emulsions result, because of antagonistic action of the two kinds of emulsifying agents. An excess of casein causes oil-in-water emulsions to form, and a deficiency of casein results in water-in-oil emulsions. Dextrin¹⁵⁷ is another emulsifying agent employed for oils immiscible with water. A thin paste is made of dextrin mixed with water, compounded with the oil, and vinegar stirred into it to form a homogeneous mass. Also, dextrin may first be mixed with the vinegar and the oil added afterward.

Thomson-Houston Co., Ltd.⁴¹⁵ states that an emulsion is formed when an oily substance and a soap-like emulsifier or casein are mixed together without water, heated to 150° and then added to the water phase.

Knaggs,²⁸¹ discussing the results of his work on the effect produced by the replacement of the amino group by a hydroxyl group in a protein, points out that the protein gelatin in this case becomes a more efficient emulsifying agent. But, when it is converted into the methylene-amino

group, an opposite effect is obtained. Thus the emulsifying efficiency of a protein for oil and water seems to be considerably altered if the active groups present in the molecule are changed, either by substitution or addition of another group. The deaminizing of gelatin with nitrous acid increases its emulsifying power for oils, provided the solution is not so dilute that the viscosity falls below the optimum value indicated by Holmes and Child.¹⁶⁶

Roberts and Smith³⁷⁵ emulsified fuel oil or coal oil mixtures in a colloid mill with about 4 per cent of nitrogen monoxide, using casein or starch as the emulsifier. A small proportion of soluble or insoluble borosilicate and sodium chloride may be added to control combustion and facilitate ignition.

The Hull Co.¹⁷⁷ developed a new emulsifying and stabilizing agent for all types of oil-in-water emulsions. The product is neither acid nor alkaline and gives a smooth, stable emulsion which is equal in quality to those produced with a colloid mill. Stratford (Texas Co.)⁴⁰⁷ prepared emulsions by using either sodium soap or finely divided fuller's earth as an emulsifying agent.

Electrolytes

The Asphalt Cold, Ltd.¹³ emulsifies bitumen, using 2 per cent of oleic acid, mixing with vigorous stirring at 100-110°, adding a 5 per cent solution of alkali silicate or borate, and finally washing with hot water. Levy^{297,298} claims that an aqueous bitumen emulsion is obtained by using an aqueous alkali silicate solution. Complete emulsification follows without the addition of a fat and the process must be carried out continuously. Emulsifying agents⁵³ are prepared by treating a low-temperature tar or its fractions with phosphoric acid, or other acids, and using a purified oil as a diluent. Findlay¹²² prepared a bitumen emulsion by shaking lime with water, heating, and introducing slowly with stirring a mixture of hot bitumen and alum solutions.

Tfol's⁴¹¹ emulsifier consists largely of silica, used as a substitute for soap by the Arabs of northern Africa, which not only absorbs oil, but strongly emulsifies oil in water. According to Rütgerswerke A.-G. (Kahl),³⁷⁸ bitumen emulsions are made of a melted coal-tar or petroleum tar stirred with a pasty mixture of alkali-reacting substances, such as iron, aluminum and zinc oxides and basic magnesium salts. Kripke²⁸⁸ proposed a method for treating solutions with such proportions of acids or acid salts that the emulsion formed is not broken when an acid is added. The percentage of acid that may be added to an emulsion depends upon that used in its preparation. Thus, with about one per cent solution of hydrochloric acid, the emulsion remains stable as long as the acid added is less than 11/12 mols. Instead of soap solutions, water-soluble salts of pure fatty acids or mixtures of these salts may be used.²⁸⁹ Holmes and Williams^{107a} use iodine as an emulsifying agent. Ether, amyl alcohol, ethyl acetate or amyl acetate give an emulsion on shaking with water if a one per cent iodine solution is added to the water. These investiga-

tors assume that a film of adsorbed iodine is formed in the interface. Holmes and Williams state that they failed to obtain an emulsion with iodine in the presence of an excess of potassium iodide in the water. Thus iodine alone is best as an emulsifier.

Hanseatische Mühlenwerke¹⁵³ recommend the use of solid alkali instead of aqueous alkali solutions for preparing emulsions. Böhm and Haas³⁷ prepare an emulsifying agent by mixing lubricating soap and starch and adding finely divided potassium hydroxide. The Distillers Company, Ltd. (Langwell)¹⁰³ prepares aqueous emulsions by dissolving substances to be emulsified in organic solvents, such as amyl or butyl alcohol, ketones, esters, or Turkey-red oil, and adding salt solutions, such as sodium acetate or sodium chloride. The Chemische Fabrik vorm. Westend⁶⁹ indicates that hydrocarbon emulsions may be prepared by heating hydrocarbons with mineral acids containing anhydrides, especially sulfuric acid or sulfurous acid, at temperatures at which the reaction product separates on top of the sulfonic acid and emulsifies to form stable emulsions. Berend³¹ patented emulsion preparations from hydrocarbons, cresol, pitch, resins, tar and asphalt, in which a small proportion of concentrated waste sulfite liquor in water is used as emulsifier, to which is added gradually the insoluble substances to be emulsified, the resulting mass being agitated. McElroy³⁰⁵ prepares stable emulsions from linseed oil, tar oils, etc. The increased emulsifying power is due to the sulfite liquor preparation which contains a small percentage of a sulfonated oil or a hydrocarbon as a protective colloid, as well as a small proportion of dissolved soda sludge.

Knopf's patent²⁸² refers to the conversion of certain solid or liquid substances into clear emulsions. The conversion is effected by oleic acid, which is saponified in the presence of alcohol, without heating, by means of a quantity of alkali insufficient for complete neutralization, and then mixed with the substances to be emulsified, with or without the addition of mineral oils or petroleum. Such oils may emulsify benzene, salol, thymol, naphthol, menthol and naphthalene. For example, 40 parts of oleic acid and 8 parts of 50-per cent caustic alkali solution are stirred into 20 parts of alcohol and naphthalene.

McBain and Woo^{304a} investigated spontaneous emulsification occurring in certain systems without the assistance of mechanical means. A paraffin oil containing one gram of lauric acid, on cautious introduction of a layer of 1/20*N* sodium hydroxide, emulsified spontaneously. After a few days the system was centrifuged, and three layers containing all three components were obtained. These layers were a transparent sodium hydroxide, a paraffin-oil layer, and a milky turbidity. The effect may be demonstrated clearly by adding a dyestuff such as eosin to the oil. This type of emulsification is believed to be caused by local movements attributed to a decrease in the surface tension. On the other hand, collisions of diffusing molecules are of great influence.

Colloids

Beijerinck²⁵ states that emulsion formation may take place by mixing aqueous solutions of certain gelatinous colloids. Thornley, Tapping and Keynard⁴¹⁶ heat petroleum or carbonaceous tarry pitch until liquefied and then add a hot, aqueous colloidal suspension of cellulose in a water-soluble alginate containing an alkali, such as ammonium hydroxide. The aqueous suspension is maintained at a temperature corresponding to the boiling point. Bender and Loesch^{26,27} emulsified two immiscible oils, such as castor and pure paraffin oil, in a hydrosol. Stiff, stable paraffin emulsions result. Kirschbraun²⁷⁶ adds liquefied bitumen to a suspension of clay in water, and stirs the mixture at a temperature which prevents clumping; or the stiff emulsion is treated by a suitable method in order to liquefy it.²⁷⁷

Some patents²⁷⁸ are concerned with the preparation of aqueous bitumen emulsions with bentonite. A preliminary investigation of the use of bentonite as an emulsifier for kerosene, red engine oil and furfuraldehyde has been carried out by English.¹¹⁶ He states that emulsions made with tap water were more stable than those made with distilled water, when bentonite is used as the emulsifier. The fact that bentonite is a sodium clay yielding comparatively large percentages of sodium hydroxide on hydrolysis and capable of undergoing a base exchange in the presence of magnesium and calcium salt solutions suggests that it acts as an emulsifier, promoting the oil-in-water type of emulsion, especially in the case of sprayed emulsions.¹¹⁷ At the same time, bentonite acts as a water softener and, therefore, is useful in cases of permanent hardness. Regarding cresylic acid, dual types of emulsions have been obtained. The principal objection to bentonite as a practical emulsifier and water softener is its impermeability to water.

It is said⁵⁸ that Wyoming bentonite is widely and successfully used for stabilizing emulsions of many substances immiscible with water. Bentonite is more stable than soap because it is less affected by chemical changes in the solution. Four forms of Volclay bentonite are available for use in the preparation of emulsions, namely, fluid, paste, powder, and dry solid. For practical purposes, bentonite is prepared as a liquid paste or gel, as thick as stirring or mixing will permit, about 10-12 parts of bentonite to 90 parts of water. Bentonite is used in the manufacture of asphalt emulsions, that is, dispersions of asphalt in water. A stiff consistency of bentonite is desirable, because in mixing with the emulsion it counteracts the natural tendency of asphalt to coalesce. In the preparation of an asphalt emulsion, the bentonite paste or gel is heated and the hot asphalt poured into it in a thin stream with continuous stirring. The final proportions of a fairly thick emulsion are 10 parts of bentonite, 90 parts of water and 250 parts of asphalt.

The Chemische Fabrik vorm. Wiernick A.-G.⁷⁰ suggests substances such as clay, fuller's earth and colloidal iron hydroxide as emulsifiers. They are added with stirring, the colloidal compounds breaking off on heating. Not only the emulsifier itself, but also the conditions under which

it is added are of great importance in the preparation of emulsions. Grundlach¹⁵¹ prepares emulsions by using melted bitumen mixed with a colloidal suspension in a container under pressure higher than atmospheric; depending on the resulting mixture, the pressure may be still higher.

Nohl³²⁷ patented an emulsifying agent obtained by kneading finely divided substances free from fats and rich in proteins, drying, and moderately heating until clots formed; large proportions (about 40 per cent) of highly concentrated sodium hydroxide solution were used, without the addition of water. The emulsifier so prepared may be used as an intermediate constituent of soap to increase its emulsifying action.

Delco Co. (Walsh⁹⁵) recommends using dry, finely divided alginates as emulsifiers. These alginates are soluble in water, and their viscosity remains unchanged. Kadmer²⁷³ discusses the application of soap, Turkey-red oil, triethanolamine and lanolin as emulsifiers. Barne's¹⁹ considers lanolin to be well suited for emulsification after treatment with a mixture of ethyl acetate and alcohol, separation of the insoluble substances, and evaporation of the solution. Uddeholms Aktiebolag (Mayer⁴¹⁰) succeeded in emulsifying with oil of turpentine by mixing the components of an aqueous emulsion at high temperature.

Kadmer²⁷⁴ suggests emulsifiers such as soaps, lanolin and other emulsifying agents for the emulsification of systems containing oils, fats, waxes and resins. Hubmajer¹⁷⁶ prepares stable aqueous emulsions from hydrocarbons, oils and waxes by using as emulsifiers proteins, agar-agar and saponin, which decrease the interfacial tension, and gum arabic or tragacanth, which increase it. Glue and starch pastes are considered especially suitable, and the addition of borax or Glauber's salt for stabilizing is recommended. The Deutsche Hydrierwerke A.-G.⁹⁷ use dihydrodioxylene in their emulsification method, together with soaps or soap-like substances, such as resin soaps, Turkey-red oil and organic sulfonic acids. The Imperial Chemical Industries, Ltd.²⁶⁴ prepare aqueous emulsions from strongly sulfurized linseed oil by using as emulsifiers small proportions of tannin, gallic acid, or tannic acid. The Imperial Chemical Industries, Ltd. (Hailwood, Shepherdson and Stewart²⁶⁶) make aqueous emulsions by mixing the substances to be emulsified with gelatin, gum arabic, or urea, dissolved in thiourea or alkaline nitrate solutions. Knaggs²⁸¹ claims that deaminized gelatin of various origins is a good emulsifier. Woodman⁴⁴⁰ used lecithin as an emulsifier in preparing emulsions of (1) hydrocarbons, chloroform, carbon tetrachloride, olive oil and linseed oil; (2) oleic acid; and (3) anilin and its homologs and phenol. The first produced dual emulsions; the second, water-in-oil emulsions, and the third, oil-in-water emulsions. Latimer-Goodwin Chemical Co. (Goodwin²⁹⁵) used casein admixed with gamboge and alcohol, as well as an alkaline agent, such as soda. Canadian Industries, Ltd. (Banbury and Clark⁵⁶) prepare emulsions of sulfurized fatty oils by sulfonating at high temperature, adding 0.5 per cent tannin or gallic acid, and mixing the product with a slightly alkaline casein solution.

The Chemische Seifenfabrik vorm. R. Baumheier A.-G.⁷⁴ suggests

preparing emulsifiers either by mixing alkalies or the ammonium salt of casein with resins, as well as with fatty-acid soaps, or by simultaneous saponification of casein and resins with alkalies, especially ammonia, which swells casein. After stirring until a viscous mass is formed, the emulsifier is subjected to ripening for many hours. Woodman,⁴⁴² discussing the use of proteins and related substances as emulsifiers for phenolic solutions, points out that proteins, protein-containing substances and their decomposition products yield two types of emulsions with phenols. The oil-in-water type is formed only with a hydrocarbon, such as toluene. Woodman believes that the formation of gels in certain systems is indicative of the fact that the presence of water is necessary before emulsoids can emulsify, because their swelling in water is essential.

Brown and Lum⁵⁰ prepare agar agar-paraffin emulsions by using as emulsifier a mixture of one g sodium acid carbonate, 2 g tragacanth and 6 g gum arabic in 30 cc glycerin and 1.7 g agar-agar dissolved in 80 cc boiling water, added with stirring. Woodman^{441, 443} used toluene, chloroform, carbon tetrachloride, oleic acid and various lecithin preparations for emulsifying light petroleum, explaining the presence of both types of emulsions by the active substances present in the emulsifier used. The Sociedad Anonima Papeteries Navarre³⁹⁴ prepares emulsions of a dry oil by using an alkali resinat solution treated with ammonium sulfate. Deiglmayr^{90, 91} recommends the use of pectin or pectin-containing substances in the presence of fructose, sucrose, or mannose in the preparation of highly concentrated, stable, aqueous emulsions of oils, fats and waxes.

Vishnevskaya and Kniga⁴²¹ investigated the emulsifying ability of benzene in water with agar-agar, saponin, albumin, pectin, gelatin, lecithin and casein. By plotting in triangular coördinates, emulsification and coagulation ranges were obtained. High concentrations of sugar were found to favor emulsification, but two of the emulsifying agents, *i.e.*, lecithin and casein, decreased the stability of the emulsion under certain conditions. If emulsifiers are arranged according to their ability to emulsify, the following sequence for decreasing emulsification is obtained: agar-agar, albumin, gelatin, saponin, casein and pectin. With regard to the minimum concentration necessary to produce an emulsion, the sequence is as follows: saponin, casein, gelatin, agar-agar, pectin and albumin. In the first series, the height of the emulsion layer in the graduate serves as a measure of its emulsifying ability, while in the second series, emulsification is calculated from surface-tension measurements taken at the liquid/liquid and liquid/gas boundaries.

Ermolenko and Guterman report a study on the emulsifying action of bile on different systems such as benzene-water, sunflower oil-water, fish oil-water and paraffin oil-water, as well as of egg-yolk on the system benzene-water at 15°. Both readily effect emulsification. In the case of bile, the action is greater the difference in polarity of the two immiscible liquids.^{118a}

Many data regarding hydrophilic colloids which may serve as emulsifying agents have been recorded in the literature. Among the most com-

monly recognized solid emulsifying agents of this kind are: basic salts of iron, copper, nickel and aluminum, lime, hydrated iron oxide, arsenous sulfide, silica, calcium sulfate (plaster of paris) and clay. Carbon black, soot and mercuric iodide may be considered as hydrophobic emulsifiers. When an emulsion is formed with a hydrophilic emulsifying agent, the addition of the proper percentage of a hydrophobic agent breaks it down. When both types of emulsifying agents are present in equal proportions, one neutralizes the emulsifying action of the other. The free carbon contained in tar is the emulsifying agent which causes the formation of emulsions in which water is the disperse phase. The resistance of emulsions is not the same for all tars with a given percentage of free carbon. The emulsifying effect of carbon changes also for each of the oil constituents, as well as for water. In general practice, it is known³²⁶ that the most stable emulsions are formed from tars containing the largest percentage of saturated oils. There is also an optimum proportion of carbon which favors the formation of stable emulsions containing a high percentage of water. This optimum content also is not the same for all oils and tars. The finely divided, insoluble solid particles are more readily wetted by oil than by water.

Schlaepfer³⁸³ used carbon black as an emulsifier for preparing kerosene, turpentine, benzene and toluene emulsions. The order in which the constituents of the emulsion are added does not affect the product obtained. The Flintkote Co.¹²⁵ claims emulsions of bitumen, liquid or solid hydrocarbons, natural or artificial resins, waxes and stearins prepared by the addition of mineral or drying oils or fatty acids with insoluble powdered mineral substances, such as colloidal clay, as emulsifiers, to which alum was added to regulate the pH concentration. Bechold, Dede and Reiners²³ entertain the belief that the emulsifying efficiency of an insoluble powder is affected by the presence of a suitable solute in one of the liquids; for example, pure benzene is not emulsified in distilled water by a powdered clay, whereas an emulsion does result on adding a drop of pyridine, nitrobenzene, amyl alcohol, ethyl alcohol, acetic acid, sodium hydroxide, barium chloride, or sodium nitrate. Redlich³⁶⁷ states that highly concentrated aqueous emulsions may be prepared by intimately mixing a powdered inorganic gel of high absorptive capacity, such as aluminum oxide or ferric oxide, but not silicon oxide, with enough of the liquid or the solution to be emulsified to exhaust its emulsifying ability, and then stirring in water.

Resin Soaps

Collier⁷⁸ found that a soap prepared from resin to which sodium hydroxide had been added has valuable emulsifying properties. Six parts of resin are boiled in a solution of one part of sodium hydroxide for 2 hours. Cooling causes the soap to precipitate as a jelly-like mass from which the water is pressed and which is then dried on a water bath. The soap obtained is soluble in alcohol and water, and precipitates from

the solution without forming a gel. Resin soaps act more energetically than oil soaps. Coal-tar is easily emulsified by a resin soap added in alcoholic solution. Hydrocarbons⁴⁰⁹ and their derivatives, as well as mineral and tar oils, may be emulsified by resin soaps. Emulsions of an optional concentration are obtained by shaking or stirring with a small amount of the emulsifying liquid in the presence of a large amount of water, or with such a dilute alkali that the excess water is sufficient to maintain the resin soap in a stable solution. Barnold, Ltd.²¹ made a mixture of tar, pitch, or bitumen by using an insufficient amount of tar oils to dissolve a mixture of casein, resin, sodium hydroxide, and water. Goodwin's¹⁴⁶ patent deals with making emulsions with certain substances known as gum resins, for instance, olibanum (frankincense), and in particular gamboge. Gamboge is a gum resin used as a yellow pigment. Initially, alcohol is added to the oil to be emulsified, together with enough water to form a creamy emulsion. The addition of oil and water is continued until the total amount of both has been incorporated. After heating to complete saponification, the tar mixture is then added very slowly to the hot solution of the casein and resin soap.

Asphalt Cold, Ltd.¹⁴ also proposed to emulsify by means of resin and dilute alkali solutions. Texas Co.⁴¹⁰ mixed a mineral oil with sodium resinate and phenol in suitable proportions in order to produce an emulsion. Bendixen, Buchner and Uhele²⁸ used as emulsifiers salts of the higher chlorinated fatty acids, resin acids, whale oil, fatty acids, etc. Emulsification³⁹⁸ can be carried out by a small addition of resin, especially in oils of high acidity. A phenol content of about 30 to 35 per cent can be reached, which is not possible with resin soap, because poor emulsions result therefrom. Additional amounts of a phenolic oil added to an emulsion give a product miscible with water. Hart and Co., Ltd.¹⁵⁶ patented a method for preparing an emulsifying agent for all kinds of oils (animal, mineral, and vegetable). Resins, soaps, oleic acid, coconut oil, methyl or ethyl alcohol, glycerin, glue, or other colloidal substances and alkalies are used, *e.g.*, 4 parts resin (sp gr 1.004-1.1), 16 parts soap, and 8 parts methyl alcohol. The products are prepared as liquid pastes or in solid form, and diluted with water. The Königliche Stearinfabrik vorm. Gonda²⁸³ patented a dust-binding medium prepared by emulsification in water of high-melting hydrocarbons or bitumens or a mixture of both by means of resin acids, fatty acids or oxy-fatty acids or naphthenic acids. The resulting material is mixed with an emulsion which is obtained from the tar residues of petroleum refining, bitumens, etc. by using albumin substances as a dispersion medium. Thompson and McGivern^{413, 414} use liquid resin made of cellulose or sulfite and a caustic alkali. A solution of alkali is added to a mixture of liquid resin and melted bitumens and the whole is stirred together to form an emulsion. Rasser³⁰⁴ discusses savonade as an emulsifier. Savonade is a Hexalin soap, Hexalin containing an oil which by saponification turns easily into savonade, a simple and cheap emulsifier.

Water-soluble Gums

Wiernick Co. A.-G.⁷¹ use two emulsifying agents at the same time, namely, a vegetable gum and algae slime, for preparing aqueous emulsions of paraffins. Very stable emulsions result. Disney and Kernot¹⁰¹ produce emulsifying agents for tar, pitch, bituminous materials, vegetable oils and others consisting of resins or other saponifiable material and glue or gelatin, treated with dilute alkali or acid liquids.¹⁰² Stiff, stable emulsions of paraffin are obtained, according to Glücksmann,¹⁴⁴ when 70 kg of paraffin are added to a solution containing one kg of agar-agar, 25 kg of water, 0.5-1.0 kg of gum arabic swollen in water, 6-8 kg of sugar and one kg of swollen gelatin.

Organic Compounds

It is generally known that relatively highly polar and ionized constituents of oils are of most importance in determining the emulsification characteristic of an oil. If the hydrocarbon group is short, making the molecule more polar and more water-soluble, its efficiency as an emulsifying agent should be less. If the hydrocarbon group is long, making the molecule less polar and more oil-soluble, its efficiency as an emulsifying agent again decreases. Thus fatty acids and their derivatives, whose ratio of polar moment to molecular weight lies between certain limits, should be considered the most efficient emulsifying agents of their kind, which actually is the case.

Kösters²⁸⁴ patented the use of an amide of a higher fatty acid, *e.g.*, stearic acid, or an acyl derivative of an aromatic base, such as the anilide of stearic acid, as emulsifiers which, when boiled with water, are introduced into the oil or fat to be emulsified in the presence of a salt of a higher fatty acid. A complete and homogenous emulsification is obtained with either the amide or the anilide, depending upon the dilution, when the emulsion is cooled. These emulsions remain stable when cold, as well as at boiling temperatures. These emulsifiers increase the tendency of a fat to take up water, even when a small proportion of the substance is added. The limit of incorporating water is only about 20 per cent above that at which a mixture of fat and water is formed.

The I. G. Farbenindustrie A.-G.^{226, 258a} reports the emulsification of light mineral oils with water by means of soaps and hydrated phenols; wool-grease, Montan wax, acetone and sulfonated alkyl naphthalenes may also be used as emulsifiers. Richardson and Griffin^{372, 373} proposed a modified method for producing oil emulsions in the cold by adding cresylic acid or cyclohexanol. Merrill's patent³¹⁰ deals with the formation of relatively stable emulsions by compounding an aliphatic hydroxyl derivative with naphthenic soaps and dispersing the product obtained in water. These emulsions apparently retain their permanence regardless of the extent of dilution. Stable oil emulsions have been prepared, using a bismuth salt of a fatty acid dissolved in a volatile organic solvent, mixing the solution with water and oil, and removing the solvent by distillation.⁸⁴

von Boyen^{421a, 421b} first prepared Montan wax from the bitumen extracted from dried Thuringian lignite with volatile solvents.^{282a} On being distilled with superheated steam, after having been freed from the solvent, this bitumen yields under ordinary pressure a white hard mass, melting above 70°, and consisting of a mixture of fatty acids and a hydrocarbon. This hydrocarbon appears to be a decomposition product, for on distilling the extracted bitumen with superheated steam *in vacuo*, a product consisting of montanic acid and an alcohol is obtained. This alcohol, when separated from the acid by pressing from the hot solution, has been found useful as an emulsifying agent.¹⁰⁰

Hey¹⁶³ used as stabilizers a halogenated phenol, a carbohydrate, allyl alcohol, lignite, wax, glycol, glycerin, cyclohexanol, glucose, fructose and dextrin. The I. G. Farbenindustrie A.-G.¹⁸⁹ states that aryl dihydrogen phosphates or diaryl hydrogen phosphates or their salts may be used alone or with other emulsifiers to produce emulsions of non-phenolic organic compounds, in which they are substantially insoluble. For example, oleic acid in water, aniline in water, cyclohexanone and benzene in water, sodium ditolyolphosphate and sodium diercylphosphate are good emulsifiers.

Gross and Engelstad¹⁴⁹ produced emulsions of heavy hydrocarbons, such as coal tar, mineral oil, or distillation residues, with concentrated solutions of oxy-lignin derivatives, obtained by treating wood with sulphurous acid, or with the condensation or oxidation products of such derivatives. Pectin or pectin-containing substances may also be used as emulsifiers. Alkaloids, related to heterocyclic compounds, chiefly quinoline and pyridine,¹⁵⁰ are useful in the emulsification of heavy mineral oils. These hydrocarbons or carbocyclic compounds have a neutral reaction toward both acids and alkalies, which affects these alkaloids in such a manner that they emulsify without being heated when a small percentage of ammonia is added to produce a weak alkaline solution. These emulsions have a broad application, principally for mechanical purposes, such as lubricants, dust binders, etc. The quinoline or pyridine-alkaloidal bases,⁴²⁰ taken in a ratio of 1:1000, are heated in the presence of an inorganic or organic base or salt to produce a slightly alkaline reaction with the heavy hydrocarbons reduced in density by the addition of light hydrocarbons. The mixture forms a stable emulsion with water.

High molecular weight alcohols and ketones,³⁸⁶ insoluble in water, with or without hydrocarbons, may be compounded with alkali salts of tetrahydronaphthalene sulfonic acids or their derivatives. Also, by means of the alkali salts of tetrahydronaphthalene sulfonic acids, large quantities of the higher alcohols, such as cyclohexanol or amyl alcohol, may be kept in solution. These solutions will hold considerable proportions of hydrocarbons, fats, oils or resins in the form of emulsions.

According to Krannich,²⁸⁶ emulsions of organic substances, except those containing the phenolic hydroxyl group, in organic or inorganic solutions may be obtained by treating them with liquids in the presence

of aryl acid esters or phosphoric acid esters. Esters of organic acids or their substitution products with oxy-amines, as well as their derivatives, or condensation products, polyvalent alcohols and iso- or heterocyclic amines also serve as emulsifying agents. It has been claimed that oil emulsions made with these emulsifiers are not influenced by dilution, by changes in temperature, or by action of acids or lime.

Montanwerke A.-G. (Riebische ³¹³) emulsifies phenols or creosote oils, as well as crude mixtures obtained from various types of tars, with such organic bases as pyridine and quinoline derivatives, amines, and aniline. Briggs and Schmidt ⁴⁸ suggest dyestuffs as emulsifiers. Mention is made of Congo red, which has the property of forming a colloid. Perhaps it is of interest to compare its action with that of other dyes forming true or semi-colloidal solutions. The fact that methyl violet added to the water phase in a water-benzene system produces foam when agitated is considered proof that it may act also as a strong emulsifier for benzene. These investigators experimented with a one per cent methyl violet solution, but were unsuccessful in obtaining an emulsion. Although a concentration of the dye occurs in the interface, it is not suitable for the emulsion formation. It may be possible that certain dyestuffs are suitable for this purpose; but the fact that foam formation is promoted by a certain substance should never lead to the conclusion that this substance favors promotion of emulsion formation, because foams and emulsions are not identical, but are analogous only to a limited extent.

Melamid ³⁰⁹ emulsified hydrocarbons and fatty substances with aniline or its homologs either alone or mixed with hydrocarbons, soaps, soap-substitutes, or such emulsifying agents as alcohols, phenols, cresols, naphthols, cyclic hydrocarbons, or pyridine bases. Kizber ²⁸⁰ recommends a new saponifier-emulsifier for fats which, when taken in large quantity, acts as efficiently as Twitchell's and Petrow's contact catalyzer; but the fatty acids so obtained are somewhat darker than usual, except the glycerides, which are lighter. When stearic acid is distilled, some of the undecomposed fats remain as a Vaseline-like residue, which is a thick, black oil, soluble in ether and petroleum ether, and when sulfonated, forms an emulsifier. To 100 g of the residue is added in small amounts a mixture of 50 g of oleum and 50 g of sulfuric acid (sp gr 1.84) during a period of 20-30 minutes at 38-40°, and the product formed is allowed to stand over night.

Merrill Co. ³¹¹ prepared an emulsion from 80 parts castor oil, 19 parts water and one part triethanolamine. Hercules Glue Co. (Lindstaedt ¹⁰¹) produces oil emulsions using as emulsifiers the amino salts of fatty acids dispersable in the oil-phase as well as in the water-phase. The H. Th. Böhme A.-G. ¹⁷³ consider castor oil, the butyl esters of sulfuric acid, oxystearin and the fatty acid of sulfonated whale oil, as well as the isopropyl ester of ricinoleic acid, to be emulsifiers. The Gesellschaft f. Chemische Industrie (Basel ^{141,142}) use as dispersion agents the tertiary ammonium compounds of unsymmetrical acylated diamines, such as octylaminoethyldiethylbenzyl ammonium chloride or methyl sulfate.

The I. G. Farbenindustrie A.-G.²¹⁸ makes use of products, obtained by the esterification or splitting off of water from amines containing the hydroxyl group with organic carboxylic acids, mixed with soaps to produce emulsification.

The I. G. Farbenindustrie A.-G.²²¹ prepares emulsifiers by treating conversion products of aliphatic acid chlorides or anhydrides having at least 6 carbon atoms with high molecular weight oxy-fatty acids or their derivatives, and sulfonating either simultaneously or in succession. The high molecular weight aliphatic-hydroaromatic, or aliphatic-aromatic hydroxyl compounds with aliphatic-aromatic sulfonic acids containing either the hydroxyl or a halogen group, or their derivatives, may serve as emulsifiers.²²² Other patents^{202, 210, 225} deal with the preparation of emulsifiers from derivatives of polyvalent alcohols or from aliphatic-aromatic compounds with one or more aliphatic hydroxyl groups or ethylene double bonds. According to A. G. Seifenfabrik (Zürich) (Steinfels²), emulsifiers may be mixtures of high molecular weight alcohols insoluble in water or hydrated phenols, such as cyclohexanol, with high molecular weight hydrotropic aliphatic compounds having not less than 6 carbon atoms and either an oxy- or an amino-group or both, *e.g.*, triethanolamine or its salts.

The I. G. Farbenindustrie A.-G.²⁵⁰ uses mixtures of condensation products of higher fatty acids with ammonia, aliphatic or heterocyclic amines, their derivatives or substitution products and true sulfonic acids of the aliphatic or aromatic series, especially those with a high wetting and dispersion ability. The Chemische Fabrik vorm, Sandoz⁶⁴ indicate as emulsifiers those made up of mixtures of monoaryl ethers of polyvalent alcohols, such as monoaryl glycol and monoaryl glycol ether, with soaps or sulfonated oils, fats or fatty acids, salicylic acid, benzylidene anilines (Schiff's bases), or sulfonic acids. The I. G. Farbenindustrie A.-G.²⁵² considers the product of esterification of the carboxyl group in oleic acid by sulfo-acetic acid suitable as an emulsifier. A solution of a polymerized carboxylic acid, such as polyacrylic acid, or a polymerized mixture of acrylic acid and acrylic acid nitrile or styrene as an emulsifying agent is the subject of another patent.²⁵⁴

Emulsifying agents²¹¹ may be prepared by converting cycloaliphatic or hydroaromatic oxy- or halogen-sulfonic acids or their salts with high molecular weight fatty acids or their derivatives or salts in the presence of organic solvents. Emulsifiers prepared either from aqueous solutions of amines having an alkyl or cycloalkyl group with at least 8 carbon atoms, one hydroxyl group, a double bond, or an amino group in the above-mentioned compounds, or by sulfonating a mixture of aromatic hydrocarbons and aliphatic alcohols with not less than 3 carbon atoms or cycloaliphatic or aliphatic-aromatic alcohols in amounts of 2.2-4.0 mols for one mol hydrocarbon are patent by the I. G. Farbenindustrie A.-G.^{226, 227}

The conversion of higher fatty acids in the presence of acid-binding agents, such as pyridine, dimethyl aniline, or calcium carbonate, together

with aliphatic, aromatic, hydroaromatic, amino or imino sulfonic acids or their salts in solution results in the formation of emulsifiers.²²⁹ The I. G. Farbenindustrie A.-G.²³⁰ recommends as an emulsifier a crude paraffin oxidized at 70-80° with 60-per cent nitric acid, an oxidation product containing 5 per cent of unsaponifiable material being obtained. This material is saponified with sodium hydroxide under pressure at 200°, acidified and distilled twice *in vacuo* to reduce the unsaponifiable content in the product to 1.5 per cent. The esterification product of sulfo-palmitic acid with ethyl, propyl, butyl, or amyl alcohol may serve as an emulsifier.²³¹ The I. G. Farbenindustrie A.-G.²³² prepares emulsifiers by converting carboxylic acid halides or anhydrides with methyl amino sulfonic acids, their derivatives or their salts, in the presence of alkyl diluents, which results in the formation of acid amides.

Condensation or esterification of ethers of oxalylamines with high molecular weight fatty acids causes the formation of an emulsifier^{195, 199, 200}. The Imperial Chemical Industries, Ltd. (Banbury and McGlynn²⁵⁹) suggest as an emulsifier tallow esterified with polyvalent aliphatic alcohols, such as glycerin, in the presence of catalysts, and sulfonation of the product obtained in the presence of a solvent. In another patent, the Imperial Chemical Industries, Ltd. (Baldwin and Hailwood²⁶¹) prepare emulsifiers by using the alcoholate of a saturated or an unsaturated alcohol containing at least 6 carbon atoms with the alkali salt of β -halide ethane sulfonic acid. Emulsifiers are obtained, according to the I. G. Farbenindustrie A.-G. (Beller and Luther²³⁸), by chlorinating the oxidation products of paraffin hydrocarbons or waxes, alone or in a mixture. As a suitable solvent is considered one having a chlorine content up to 40 per cent of the original material at a temperature below 100°, whereby resin formation is retarded; the product is neutralized with basic reagents.

Emulsifiers are prepared from neutralized or saponified oxidation products of paraffinic hydrocarbons in which water-soluble salts are present. Agthe⁵ recommended the preparation of an emulsifier from glue-like substances, such as casein, difficultly soluble in water, which are made soluble by salts of organic sulfonic acids, carboxylic acids, and their respective salts, with the exception of pyrophosphoric acid and its salts. The Deutsche Hydrierwerke A.-G.⁹⁸ claim the polyricinoleic acid amide, arylide, as an emulsifier, as well as a stabilizer in emulsification processes. The I. G. Farbenindustrie A.-G. (Luther and Beller²⁴⁶) prepares an emulsifier from the oxidation products of liquid hydrocarbons boiling above 180°, treated with a saponifying agent. Finely dispersed soybean flour in an aqueous alkali solution containing sulfur derivatives of carbon, especially carbon disulfide, forms an emulsifier.²⁹⁶

Nishizawa and Inone,^{324, 325} discussing the emulsification ability of three types of Twitchell reagents prepared from naphthalene, benzene and phenol, respectively, pointed out its relationship to the action of different electrolytes. The Twitchell reagents prepared from naphthalene and phenol show greater emulsification capacity after addition of the sodium

salts of naphthalene and phenol, but with small percentages of benzene, the opposite is the case. The addition of glycerin, or fatty acids increases emulsification.

The Imperial Chemical Industries, Ltd. (Hailwood and Todd ^{262, 263}), proposed an emulsifier for the dispersion of mineral oils and fats consisting of quaternary ammonium salts containing the alkyl or alkylene radicals with at least 10 carbon atoms and the organic hydroxyl group as contained in dodecyl, tetradecyl, hexadecyl, or octadecyl ammonium halogenide. According to Goldthwait,¹⁴⁵ oils can be emulsified with a strong soap solution, calculating 40 per cent of the latter to the amount of fatty acids designated. Hexalin in soap solutions effects emulsification.^{365, 366} The I. G. Farbenindustrie A.-G.²⁰⁵ use as an emulsifier the product obtained from 95 parts monoethanolamine sulfuric acid ester dissolved in 200 parts of water, 110 parts of 50-per cent sodium hydroxide, and 190 parts of stearic acid chloride mixed together at 10°, the sodium salt of stearic acid oxyethylamide sulfuric acid ester, of the formula $C_{17}H_{35}CO.NH.CH_2.CH_2.O.SO_3Na$, being obtained.

The I. G. Farbenindustrie A.-G.²⁰⁶ prepares emulsifiers by the condensation of the halogenated fatty acid halides having at least 10 carbon atoms with a compound of the general formula $HN(X)-R_1Y$, or $OH-R_1Y$, where X is hydrogen or an alkyl-cycloalkyl, aryl, or an aralkyl group; R_1 , an alkyl-cycloalkyl or an aryl group, and Y , a sulfuric acid ester or a sulfonic acid group: for example, the sulfo-ester of the formula $C_{17}H_{31}Cl_4CO.NH.C_2H_4O.SO_3H$, corresponding to the fatty acid compound of the general formula $R.CO.N(X).R_1Y$, or $R.CO.R_1Y$, in which $R.CO$ represents the fatty acid group; at least one halide atom is introduced into the fatty acid group, the stearic acid being chlorinated to tetrachlorostearic acid chloride, condensed with monoethanolamine sulfuric acid ester and stirred with a dilute sodium hydroxide solution.

Higher alcohols and ketones, alone or in combination with hydrocarbons, or with alkaline-reacting salts, such as alkali carbonates, borates, or silicates, together with the salts of aliphatic sulfonic acids, are considered as emulsifiers.⁹⁹ Hunddiecker and Vogt¹⁷⁸ claim as dispersing agents non-substituted hexamethylenetetramine alkylates, or arylates with any desired acid ion, to produce emulsions in hard water. Hexamethylenetetramine combines with halogen alkyls or aryls to form addition products, the behavior of which indicates a constitution of salt-like type. In most cases they dissolve readily in water and as typical electrolytes are almost completely dissociated therein. In such a case the halogen plays the part of the anion and can be readily exchanged for other negative ions, *e.g.*, sulfate, nitrate, acetate, benzene sulfonate, etc. Resinous Products and Chemical Co.³⁶⁸ prepares an emulsifier by condensing an aliphatic hydroaromatic or naphthenic carboxylic acid amide containing from 8 to 30 carbon atoms with formaldehyde and a secondary amine having less than 7 carbon atoms, by heating in an inert solvent, dioxan, in the presence of a basic catalyst, such as sodium carbonate.

Bennett³⁰ makes an emulsifier from glycol or ethylene glycol esterified with fatty acid containing at least five carbon atoms, especially stearic acid in excess, in the presence of an alkali catalyst. The Chemische Fabrik vorm. Sandoz⁶⁷ claims as an emulsifier a mixture of isomeric monoxymylenyl glycol ethers obtained by the action of glycol monochlorhydrine on a mixture of isomeric xylenols, *n*-butanol, and a sulfonating agent. The mixture of monoxymylenyl glycol ethers is treated in one of two ways: (1) first with a sulfonating agent, the reaction product being condensed with *n*-butanol, or (2) first condensed with *n*-butanol, the condensation product being treated with a sulfonating agent. The emulsifier is a brownish, viscous liquid soluble in water, with a neutral reaction.

The I. G. Farbenindustrie A.-G.²³⁵ considers ketones prepared from high molecular weight unsaturated acids as material for obtaining emulsifiers. Emulsifiers²¹³ also may be obtained from urethanes containing either hydrogen atoms in their nitrogen group; or aliphatic, cycloaliphatic, aromatic, heterocyclic, or alcohol radicals with one or more double bonds or three single bonds; or aromatic or heterocyclic rings.

Triethanolamine alone, or in combination with oleic acid, acts as an emulsifier in various emulsification methods.^{129,335} Wilson⁴³³ claims that triethanolamine, as the basic constituent of soaps, is well adapted for the emulsification of soluble mineral oils, vegetable oils, animal oils and waxes. Triethanolamine is an organic base related to ammonia. Like ammonia it reacts with acids in molecular proportions to form salts, *e.g.*, triethanolamine chloride, $\text{NH}(\text{C}_2\text{H}_4\text{OH})_3\text{Cl}$, showing that only the amino group is alkaline. Triethanolamine differs from ammonia in several respects; namely, it is a high-boiling liquid, mildly alkaline and very soluble in organic solvents. When an oil solution of a fatty acid is added to a water solution of triethanolamine, an emulsion is formed immediately. About 6 to 20 per cent of the fatty acid, including any free fatty acid naturally occurring in the oil, is dissolved in the oil and the solution mixed with a 2- to 8-per cent water solution of triethanolamine.

Orelup³⁴² prepares emulsifying agents by treating the hydroxyalkylamides derived from monoethanolamine, monobutanolamine, or monopropanolamine and fatty acids containing 10 to 18 carbon atoms with an amount of monohydrated sulfuric acid at least equal to, but not exceeding, twice the amount of the hydroxyalkylamide at 30-35° C. Fatty acid mixtures, in which fatty acids with 10 to 18 carbon atoms predominate, may replace the fatty acids. Other sulfonating agents may replace the sulfuric acid, provided the corresponding stoichiometrical proportions are used.

Sulfamides, originating from high molecular weight aliphatic sulfochlorides by the action of ammonia or amines of the aliphatic series, serve as emulsifiers in various industries.²⁰⁷ Bratke^{42,236} recommends beechwood tar distilled at 200°, benzoic acid, sodium salicylate, cresol, xylene, guaiacol, or creosote as emulsifiers for aqueous emulsions of oils, fats,

waxes, resins and asphalts. Dupont^{107,108} prepares emulsifiers by: (1) esterification of abietinic acid or its salt with halogenated alkyl or cyclo-alkyl sulfonic acid; and (2) by treatment of high molecular weight unsaturated aliphatic hydrocarbons containing not less than eight carbon atoms and having a stable bond with a sulfonic acid halide in the presence of a catalyst which transfers the halide. The product obtained is treated with a hydrolyzing agent.

Kropfhammer²⁹⁰ prepares emulsions from monoglycol ether in combination with soaps converted into water-soluble form. In the same patent, it is also claimed that 100 parts of the potassium soap of linoleic acid, as well as of naphthenic acid, in a homogeneous mixture with 100 parts of butyl alcohol serve to emulsify 500 parts of mineral oil. The I. G. Farbenindustrie A.-G. (Beller and Pfaff²⁴⁴) prepares emulsifiers from mineral and tar oils. LaFarge and Chanut²⁹² use as an emulsifier a homogeneous mixture consisting of an oil, whose specific gravity is less than that of the substance to be emulsified, and a solvent, like trichloroethylene, chloroform, carbon disulfide, carbon tetrachloride and an aqueous solution of ammonia; nicotine, *p*-dichlorobenzene and nitronaphthalene may be added likewise.

Stable water-in-oil emulsions are claimed¹⁷⁵ to be obtained with a mixture of emulsifiers, one component of which has a colloidal cation and the other a colloidal anion. Emulsifiers of the first kind are quaternary ammonium compounds, such as salts of pyrimidine and long-chain aliphatic ammonium compounds, as well as alkyl isothiourcates. Emulsifiers of the second kind are high molecular weight aliphatic sulfonated products, fatty acids, carboxylic acid, or aromatic sulfonic acids of capillary-active nature. For example, 700 g of paraffin oil are dispersed in the cold in water with 140 g of the alkali salt of dodecylsulfuric acid ester in a rotary stirrer, and a 40-per cent solution of technical lauryl pyrimidine bisulfate added until the pasty mixture becomes viscous. Either a positive or a negative charge is given to the final product, after driving off the water by heating, by adding one or the other of the dispersing agents.

Bratke⁴³ uses, as emulsifiers for preparing aqueous emulsions, mixtures of benzoic acid, sodium salicylate, cresol, xyleneol, guaiacol and creosote dissolved in water to which 0.01 per cent of an alkali has been added. Naphthenes obtained by destructive catalytic hydrogenation at 750° F under 3500 lbs/sq in pressure are especially suitable for the preparation of emulsifiable oils, such as Colombian or Pecos. When 90 g of the resulting product is mixed with 2.5 g of triethanolamine oleate and 7.5 g of oil-soluble sulfonate, an emulsifiable oil is obtained.⁴⁰¹

According to Harris,¹⁵⁵ non-alkaline, aqueous oil emulsions may be obtained by using as emulsifiers the esters of hydrophilic compounds of the general formula $(RO)_vX(OH)_w$, where R is an alkyl group with at least six carbon atoms, and X, either a polybasic or an etherified aliphatic alcohol with at least four carbon atoms, such as glycol, mannitol, sorbitol, etc. Compounds such as (1) monostearylglycol, (2) monostearylglycerol, and (3) diglycerol correspond to this formula whereby

the hydrophilic property increases according to sequence, *i.e.*, from (1) to (3), because of the accumulation of hydroxyl groups, whereas for (4) monolauryl, (5) monostearyl, and (6) monomellissylglycerol, the hydrophilic property decreases as a result of an increase in the length of the chain.

In another patent,^{111,112} the sulfuric acid ester of an aliphatic alcohol with more than eight carbon atoms in the form of heavy metal salts of lead, aluminum, and tin serves as an emulsifier for water-in-oil emulsions. The first of these to be considered are the sulfuric acid esters of lauryl, myricyl, and cetyl alcohols used in an amount of 0.05-2.0 per cent of the oil. For example, a solution of 0.25 cc of lead acetate in 48.75 cc of distilled water is stirred with a solution of one cc of lauryl sulfuric acid ester in 31 cc of paraffin oil. If emulsification is effected by heat, emulsions of vegetable and mineral oils, as well as of asphalt, may be formed.

The Chemische Forschungsgesellschaft m.b.H.⁷² prepares an emulsion from an unsaturated compound which can be polymerized by mixing with an aqueous solution containing as emulsifying agents methyl cellulose, ester-like compounds, ethers, or acetals of polyvinyl alcohols, such as polyvinyl acetate, having a saponification number of 80 to 100. A non-saponifying substance may be added before the emulsion is subjected to polymerization.

As emulsifying agents were proposed²⁰⁸ alkali salts of products obtained by the condensation of alkylated aromatic hydrocarbons having at least four carbon atoms in the alkyl or cycloalkyl group with an active functional derivative of an acid having the formula $\text{HOOC}(\text{CH}_2)_n\text{COOH}$, where n is 2, 3, or 4, and the keto group in the carboxylic acid so obtained is reduced. Acids of the formula $\text{RA}(\text{CH}_2)_n\text{COOH}$, where R is an alkyl or a cycloalkyl group of at least four carbon atoms; A, an aryl group, and n , 3, 4, or 5, are obtained. These may be hydrogenated; thus A is converted into a hydroaryl group. Acids of the formula given in which both R and A are hydroaryl groups may also be obtained from arylated aromatic hydrocarbons in which the two aryl groups are hydrogenated simultaneously. Anhydrides, chlorides, or acetyl chlorides may be used as functional derivatives, subsequent saponification being necessary in the case of the latter. As examples may be cited (1) butylbenzene or succinic anhydride, heated in tetrachlorethane in the presence of aluminum chloride, yields γ -4-butylphenyl- γ -oxybutyric acid, which is reduced with hydrogen in the presence of a nickel catalyst to yield γ -(4-butylphenyl)-butyric acid; and (2) cyclohexylbenzene treated as in (1), and yielding γ -4-cyclohexylphenyl- γ -oxybutyric acid and γ -(4-cyclohexylphenyl)-butyric acid.

Lundsgaard³⁰¹ produces agents for stabilizing aqueous suspensions or emulsions. Esters containing at least one non-replaceable hydroxyl group of a polyhydric alcohol and a higher fatty acid, which have been polymerized and/or oxidized before or after esterification, with purification of the acids in the intermediate stage, are claimed as emulsifiers. The product

obtained is saponified and the fatty acids are separated and heated at 180° for 10 hours with an excess of anhydrous glycerol which is removed at the end of the process, potassium soap being used as a catalyst.

Stable oil-in-water emulsions of mineral oils and/or tar oils, which possess a high interfacial tension against water and are not polar in nature, are obtained when the oils are emulsified in water in the presence of large proportions (above 10 per cent) of an oxalkyl amino salt (a product obtained by the action of sulfuric acid upon polymerized fatty acids, such as ricinoleic acid or dioxystearic acid), or of polymerized naphthenic acids. The emulsification is undertaken successfully in the presence of substances which are soluble in both phases which decrease the interfacial tension, *e.g.*, glycerin, Tetralin, ethylene glycol, gelatin, or Hexalin. In such a manner an emulsion is obtained in which the greatest part of the oil is dissolved in the closed phase. By dilution with water, stable emulsions are formed, and are not resolved by boiling. The emulsions may contain 50 to 60 per cent by volume of oil.^{428a} The Glyco Products Co. produces a low-priced, soapless emulsifying agent, under the name of "Glycoride," which is a glycol-glyceryl stearate, and "Lanosyn," a lanoline substitute which forms with water stable, light-colored emulsions of the water-in-oil type.

Sulfonic Acids and Sulfonated Oils

Sulfonic soaps which are sludge sulfonates and alkali-metal salts of sulfonic acids, characterized by their solubility in water and insolubility in ether and petroleum hydrocarbons, are used as emulsifiers. The reason for employing sludge sulfonates lies in the fact that the presence of substantial proportions of an electrolyte in the water is permissible, since with these soaps the tendency to prevent emulsification or to break the emulsion formed is less than with other soaps. Natural and artificial asphaltic materials, coal tars, petroleum and shale-oil distillates, and even waxes such as paraffin may be emulsified in water by using these sulfonic soaps.²⁶⁹ Oil may be emulsified with water if sulfur trioxide is used as an oxidizing acid and the oil is treated with it until the oil layer above the acid tar has obtained the desired properties. The temperature (100-120°) must be so high that sulfonation occurs, but carbonization of the oil is to be avoided. The yield of water-soluble oils is 80-90 per cent.²⁶⁸ An emulsifying agent¹¹⁸ is prepared by treating suitable fatty substances, such as cottonseed oil, castor oil, tallow, wool grease, or fish oil with sulfuric acid, at a temperature above that permissible in the production of sulfonated oils. The product is preferably washed with a salt solution (one per cent by volume) until it is free from acid. The emulsifying agent obtained may be modified by substances, such as sulfuric acid anhydride, added in small amounts either during its formation or afterward. This emulsifier is recommended for the preparation of tar-oil emulsions.

McElroy^{305, 306} points out that the emulsifying power of sulfite cellulose waste liquor, preferably the neutralized liquor, is increased by add-

ing a small percentage of a sulfonated oil or hydrocarbon. Caustic soda sludge from petroleum refining acts especially as a protective colloid. It has been claimed⁴⁹ that an emulsifying agent may be prepared from castor oil which is polymerized by heating to 240°, the sulfonated product being washed with water containing formaldehyde, in an inert atmosphere, and neutralized by the addition of ammonia. Nohl³²⁸ states that "Nekal," a sodium salt of a naphthenic sulfonic acid, may also be employed as an emulsifier. Matti,³⁰⁴ in preparing aqueous emulsions of bituminous substances, mixed the bitumen material to be emulsified with a fatty oil which had been treated with concentrated sulfuric acid. Petrow^{349,350} claims sulfo acids as emulsion-forming substances. Hutton and Fulton¹⁸⁴ emulsified a liquid or a melted bituminous substance with an emulsifying agent which is a sulfonated fatty oil or fat neutralized with an aqueous solution of an alkali or ammonia taken in an amount just sufficient for this purpose. In carrying out this process the neutralization of any free sulfuric acid, mixed organic acids and glycerides present in the sulfonated product, is effected *in situ* during the formation of the emulsion. The proportion of alkali used may be varied, but is usually comparable with that used in the final stage of the manufacture of sulfonated oils. According to Maag,³⁰² water-soluble tar emulsions are obtained by emulsifying the tar oils with a concentrated aqueous solution of an alkali salt of a sulfo acid in a vegetable oil. For example, 30 parts of tar oil are emulsified with one part of sodium hydroxide, 6 parts of Turkey-red oil, and one part of lubricating oil.

Sulfonated Products

Limburg²⁹⁹ recommends preparing water-soluble emulsifiers or stabilizers by sulfonating high molecular weight aromatic compounds, or mixtures, with sulfuric acid. The I. G. Farbenindustrie A.-G.¹⁸⁵ prepares emulsifiers by converting products of oxyamines with high molecular weight carboxylic acids or sulfonic acids into salts, acid amides, or esters. The H. Th. Böhme A.-G.¹⁷¹ patented as emulsifiers the sulfonated products of lauryl and myristyl alcohol. Depending on conditions existing, either the true sulfonic acid or the sulfuric acid ester is obtained. Sulfonation and simultaneous condensation of alcohols, aldehydes, or ketones by means of sulfonating agents, as, *e.g.*, 50 parts paraformaldehyde and 54 parts octadecyl alcohol stirred into 400 parts monohydrated sulfuric acid at room temperature and at 50° for 5 to 6 hours until water-soluble, is claimed as a method for preparing emulsifiers.²¹⁷

Sulfonating the oxidation products of solid or liquid paraffinic or naphthenic hydrocarbons, such as olefins, alcohols, or natural and artificial waxes, with sulfur trioxide until the resulting product is water-soluble, pouring on ice, and neutralizing with sodium hydroxide results in the formation of emulsifiers.²¹⁹ Another patent of the I. G. Farbenindustrie A.-G.²²⁰ concerns itself with the preparation of emulsifiers by the introduction of sulfuric acid groups into aliphatic, cyclo-aliphatic, or aliphatic-aromatic oxy-ethers in the presence of solvents or diluents, or

by the introduction of phosphoric acid ester groups. The H. Th. Böhme A.-G.¹⁶⁸ patented as emulsifiers alkyl or cyclo-alkyl esters of aromatic sulfonic acids alone and together with aromatic sulfonic acids, sulfonated oils, soaps, or fatty acid solutions, as well as with ketones or aqueous dispersions of esters. Energetic sulfonation of aliphatic olefins having not less than 8 carbon atoms and at least one double bond at the end of the hydrocarbon chain is recommended in a patent issued to the I. G. Farbenindustrie A.-G.²²³

The latter ²²⁴ claims as emulsifiers products obtained by treating saturated or unsaturated compounds with alcoholic hydroxyl groups and compounds containing more than 8 carbon atoms, with low molecular weight aliphatic acids containing the SO_3H group, or able to absorb this group. The H. Th. Böhme A.-G.¹⁷² suggest as emulsifiers and foam-formers, substances consisting of the higher alcoholic esters of sulfuric acid obtained by the reduction of fatty acids, particularly those sulfonated at 0° . In another patent the H. Th. Böhme A.-G.^{169, 192, 193, 194} uses as emulsifiers the sulfonation product of lauryl alcohol. Beer ²⁴ uses as emulsifier a product obtained by the condensation of a chlorinated polynuclear hydrocarbon in a solution of either sulfuric acid or fuming sulfuric acid and taken in an amount not exceeding 10 per cent of the chlorinated hydrocarbon. The reaction product is soluble in water. Hutton and Fulton ¹⁸⁷ prepared an emulsifying agent by mixing oil or sulfonated fat with bituminous material and neutralizing it with a 2-per cent solution of caustic soda.

The I. G. Farbenindustrie A.-G.^{214, 258} obtained a series of patents for the preparation of emulsifying and fat-splitting agents formed by sulfonating with sulfuric acid,²¹⁵ chloresulfonic acid, or by mixing the salt of a mineral acid or a sulfo acid with products soluble and insoluble in water, such as aliphatic or hydroaromatic hydrocarbons with more than 8 carbon atoms, in the presence or absence of diluting agents or catalysts, or in the presence of aromatic or hydroaromatic hydrocarbons or their derivatives. The I. G. Farbenindustrie A.-G.²¹⁶ proposed, in addition to an older patent ^{237, 257} dealing with the preparation of products suitable for emulsification, a method consisting of complete or partial saponification of the oxidation products of paraffinic hydrocarbons with other alkali-acting agents, such as alkali carbonates or alkaline-earth hydroxides. Liquid hydrocarbons obtained by destructive hydrogenation may be used as emulsifiers.¹⁸⁸ A method for the utilization of alkylated cellulose and organic sulfonic acids as emulsifiers has been suggested by the I. G. Farbenindustrie A.-G.^{190, 191} Clear, aqueous solutions of organic substances, slightly soluble or insoluble in water, are obtained by treating with sulfonic acids or their salts. Permanent emulsions of fats, waxes, oils, and hydrocarbons are obtained by the use of glue or gum arabic in connection with ordinary emulsifiers, such as soaps, sulfonic acids, etc.²⁰⁹

Twitchell Process Co.⁴¹⁸ prepared water-soluble sulfonic acids or their potassium, sodium, barium, calcium, magnesium and aluminum salts from

the sludge which separates out when sulfonating mineral oils. By diluting with water, unchanged oil separates out in an upper layer, which is removed, and the excess sulfuric acid is neutralized with lime.

Texas Co. (Thurston ^{410a}) patented a preparation of an emulsifier by sulfonating a mixture consisting of 60-90 per cent lubricating oil from petroleum distillate and 10-40 per cent aromatic hydrocarbons (benzene, toluene, or diphenyl). For example, 1000 parts of the lubricating oil and 400 parts of benzene are treated for many hours with 1000 parts of H_2SO_4 (98-per cent) at 150-170° F and then washed with 500 parts of water. After standing for 16 hours at 95-105° F, three layers are formed, the bottom or water-containing layer being withdrawn. After neutralization, the middle or emulsion layer gives the best emulsifier: the upper or sulfonate layer is also a good emulsifier for hydrocarbons, paraffins, or asphalts.

Oranienburger Chemische Fabrik A.-G. (Lindner and Russe ³³⁶) prepared emulsifiers made of high molecular weight, water-soluble sulfonic acids or their salts. Distillation products obtained in the refining of hydrocarbons, crude oil, or brown coal tar, together with alkalis or sodium sulfate, are subjected to treatment with sulfuric acid, a halogen hydrine, or water. Imperial Chemical Industries, Ltd. ²⁶⁵ prepared emulsions using sulfurized oils. The I. G. Farbenindustrie A.-G. ²⁴⁹ use as emulsifiers phosphate alone or together with sulfonic acids in preparing emulsions of cyclohexanol, cyclohexanone, aniline, or oleic acid in water. The Société des Produits Chimiques et Matières Colorantes de Mulhouse ³⁰⁵ states that fats, oils, paraffins, waxes, tars and resins may be emulsified with sulfite cellulose, sulfonated phenolformaldehyde products and alkylated naphthalene-sulfonic acids. The Chemische Fabrik vorm. Sandoz ⁶⁵ proposed, as a method for the preparation of emulsifiers, treatment of oleic acid-propylglycol esters with sulfonating agents.

Friesenhahn ¹³⁵ used emulsifiers consisting of mixtures of salts of sulfonated organic compounds, such as Turkey-red oil, or naphthalene-sulfonic acids, with alkali phosphates (trisodium phosphate) to which are added high molecular weight alcohols (terpineol, butyl alcohol, amyl alcohol, cyclohexanol). The I. G. Farbenindustrie A.-G. ^{86, 253} claims as an emulsifier one prepared by esterifying the alcohol of oleic acid with mono-halogenated acetic acid and converting the ester obtained with sulfurous acid. The H. Th. Böhme A.-G. ¹⁷⁴ patented, as emulsifiers, liquid esters from fatty sulfonic acids or a sulfonation product of fatty carboxylic acid esters with complete or partial substitution by the sulfonic group. The Compagnie Nationale de Matières Colorantes et Manufacture de Produits Chimiques du Nord Réunis ^{81, 82, 83} recommends emulsifiers consisting either of free sulfonic acids or their metallic salts, ammoniates, aliphatic amines, aromatics, or hydroaromatics alone or in a mixture with sulfonated oils, solvents, pectic substances, etc.

Sulfonation of saturated or unsaturated high molecular weight oxyacids or acid amides, especially those obtained from the oxidation or distillation products of crude Montan wax or from the reduction products

of its alcohols and amines, yields good emulsifiers, according to an I. G. Farbenindustrie A.-G. patent.²²⁸ The Chemische Fabrik vorm. Sandoz⁶³ prepares emulsifiers by sulfonating esters of high molecular weight fatty acids and polyvalent alcohols in which the free hydroxyl groups are replaced by halides, oxyalkyl, oxyaryl, or carboxyl groups. The Farben-Gerbstoff Werke (Flesh¹¹⁹) prepare emulsifiers by treating high molecular weight fatty acids or their anhydrides with sulfonating agents in the presence of alcohols at temperatures above 0°. The I. G. Farbenindustrie A.-G.²³⁴ halogenate carboxylic acids esters containing sulfonic acid groups or amides to prepare foaming and emulsifying agents.

Sulfonating agents act on esters containing at least one hydroxyl group in the alcohol molecule. For example, 60 parts of glycerin-ricinoleic acid ester are stirred with 80 parts of concentrated sulfuric acid at 60°, the water-soluble product obtained being poured over ice and extracted with ethyl acetate. This is the method of preparing emulsifiers advocated by the I. G. Farbenindustrie A.-G.¹⁹⁶ In another patent they¹⁹⁷ suggest preparing emulsifiers by treating olefins with sulfonating agents. For example, 100 parts of a liquid olefin mixture of a difficultly oxidized paraffin, obtained by splitting off water and carbon dioxide, are stirred with 45 parts of chlorosulfonic acid at 30-40°. The resulting product is washed with water and neutralized with alkali, ammonia, or amines. The I. G. Farbenindustrie A.-G.¹⁹⁸ use polystyrene or its alkyl derivatives as emulsifiers. They are treated with concentrated sulfuric acid or chlorosulfonic acid in the presence of solvents; this converts them into the corresponding sulfonic acids. Sulfonation at higher temperatures causes partial depolymerization.

The N. V. Chemische Fabrik vorm. Servo u. Rosenbrock^{331,332} prepares emulsifiers by sulfonation of fatty acids or their derivatives, especially esters of mono- or polyvalent alcohols, in the presence of such substances as phosphorus trichloride, which has affinity for water. Before, during, or after sulfonation, phosphoric acid, the alkyl esters of phosphorus trichloride, phosphorus pentachloride, phosphorus oxychloride, or phosphorus pentoxide are added; before or during sulfonation, isothionic, boric, or acetic acid is added. The Compagnie Nationale de Matières Colorantes et Manufacture de Produits Chimiques du Nord Réunis⁸⁰ obtain emulsifiers consisting of sulfonated condensation products,⁸³ their alkali, ammonium, or alkaline-earth salts, together with aliphatic, aromatic, or hydroaromatic amines alone or combined with other substances. The I. G. Farbenindustrie A.-G.²⁰¹ prepares emulsifiers from oxidation products obtained by partial destructive oxidation of non-aromatic hydrocarbons containing at least 8 carbon atoms, or their mixture, after separation by sulfonation of the unoxidized hydrocarbons, which contain 15-60 per cent of alcohols.

Imperial Chemical Industries, Ltd. (McGlynn and Todd²⁶⁰) prepare emulsifiers by sulfonation of shark-liver oil. The I. G. Farbenindustrie A.-G.²⁰³ recommend a method for preparing emulsifiers by sulfonating acid amides. Amides having more than two nitrogen atoms in their

molecule, or containing at least one nitrogen atom and one active hydrogen atom, or of an aliphatic nature, or consisting of aliphatic derivatives, but not alkylated amides, are brought into reaction with carboxylic acids, the resulting products being sulfonated with sulfuric acid, sulfur trioxide, oleum, or chlorosulfonic acid. The carboxylic acids must contain either a double aliphatic bond, a hydroxyl group, or an aromatic nucleus. The I. G. Farbenindustrie A.-G. (Michel and Buschman²⁴⁰) uses as emulsifier the product obtained by the action of olefins, having three or more carbon atoms, on sulfonated carbazol or carbazol derivatives, the free sulfonic acids being converted into salts. Sulfonic acids and their salts also improve the wettability with respect to water or aqueous solutions.

The I. G. Farbenindustrie A.-G. (Steindorff, Daimbar and Platz²⁴²) prepares emulsifiers from amino or imino oxyalkyl-oxyaryl sulfonic acids, the basic group of which is acetylated before or after with high molecular weight carboxylic acids, and esterifies the hydroxyl group with high molecular weight mono- or polyvalent organic acids. In another patent,^{233,241} the emulsifiers consist of urethanes obtained from alcohols containing one or two oxyalkyl groups with nitrogen, or from residual alcohol having sulfonated hydroxyl groups. The resulting sulfonated amino compounds have, in addition to the hydroxyl groups, free hydrogen atoms uniting with nitrogen to form esters of chlorofumaric acid compounds of the general formula: $RO.CO.N(X).R'.OH$, where R' is an organic group containing also the hydroxyl group combined with hexyl, lauryl, octadecyl, cyclohexyl, furfuryl, or decanol radicals; R is the aliphatic group containing one hydroxyl group combined with oxyethyl, butyl, or propyl radicals; and X is the distance of the oxyalkyl residue.

The I. G. Farbenindustrie A.-G. (Marx, Brodersen and Bittner²⁴³) prepares emulsifiers from aromatic and hydroaromatic hydrocarbons by sulfonation and converts them into magnesium salts, which in turn are replaced by mineral salts or protective colloids. Emulsifiers²⁴⁵ may be obtained from high molecular weight alkyl amines or fatty acid amides when converted into the corresponding alkyl or acyl carbamic acid chloride by phosgene and sulfonated by sulfonic acid carrying oxy- or amino-groups. Oranienburger Chemische Fabrik A.-G. (Lindner and Russe³³⁷) use as emulsifiers sulfonic acid salts of high molecular weight aromatic and hydroaromatic hydrocarbons, or a mixture of aliphatic-aromatic phenones or ketones alone or together with organic solvents. For example, the sodium salt of sulfonated oleophenone is obtained by the condensation of one mol of oleic acid chloride and 6 to 8 mols of benzene with water, free aluminum chloride, or sulfonated phenones from stearic acid or ricinic acid chloride. For condensation toluene, xylene, phenol, or tetrahydronaphthalene may be used.

du Pont (Gabelmann and Henke¹⁰⁹) applies alkali salts of sulfonic acids as emulsifiers. The I. G. Farbenindustrie A.-G.²⁰⁴ emulsifier consists of a sulfonated product obtained from the esters of a fatty acid and an oxy-fatty acid containing an oxy- group able to esterify, the oxy-fatty acid being replaced by another high molecular weight oxy-

compound of the aliphatic, cyclo-aliphatic, or hydroaromatic series. Either the condensation products of amino alcohols with naphthenes or artificial and natural resin acids, or sulfonation products are used as emulsifiers.¹⁰⁶ Oranienburger Chemische Fabrik A.-G. (Lindner and Zickermann³³⁸) prepare stable emulsions of mineral oils, neutral fats and fatty acids, using as emulsifiers a mixture of high molecular weight aliphatic or alicyclic substituted aromatic sulfonic acids or their salts, soaps, or sulfonated oils, with carbohydrates or proteins.

Deutsche Hydrierwerke A.-G.⁹⁶ use salts of thiosulfonic acids as emulsifiers. Thiosulfonic acids etherized in the α position are prepared, using organic halide compounds of the general formula $R.O.CHR'$, in which R denotes a hydrocarbon group containing at least 8 carbon atoms, either aliphatic, alicyclic, or aromatic-aliphatic; R' is an alkyl group containing one hydrogen atom and less than 4 carbon atoms, preferably the methyl group, which is converted with stable alkali, alkaline earths, or ammonium salts of thiosulfonic acid, according to the equation: $R.O.CHR'$ (halide) + $Me_2S_2O_3 \longrightarrow R.O.CHR'S.SO_3Me + Me$ (halide).

The Gesellschaft f. Chemische Industrie (Basel¹⁴³) recommends as an emulsifier the sulfonation product of castor oil. For example, 80 parts of castor oil are added with stirring to 160 parts of 90-per cent sulfuric acid at 20-25°. After standing, the mixture is washed with sodium chloride solution to neutralize the product and to adjust it to the desired fat content.

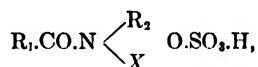
The I. G. Farbenindustrie A.-G. (Günther and Holsten²⁴⁷) claims as emulsifiers salts of sulfo-amino acids from amines, carboxylic acid amides, or nitro compounds of the aliphatic, cyclo-aliphatic or heterocyclic series with more than 8 carbon atoms in the molecule, or their derivatives or substitution products. The Oranienburger Chemische Fabrik A.-G. (Lindner and Zickermann^{339,340}) method for preparing emulsifiers involves treating mixtures of neutral fats, fatty acids and condensable lactones, alcohols and ketones with strong dehydrating agents, such as sulfuric acid, which sulfonate at the same time.

The Chemische Fabrik vorm. Sandoz⁶² manufactures emulsifiers from alkyl, aralkyl, or aryl ethers of polyhydric alcohols, condensed with mono- or polyhydric alcohols or their derivatives containing hydroxyl groups, in the presence of a sulfonating agent. For example, ethylene glycol, monotolyl or chlortolyl ether is condensed with butyl alcohol and concentrated sulfuric acid at 65-85°. Glycerol dixylyl and α -naphthyl ethers and ethylene glycol-ditolyl ether may be used.

The Chemische Fabrik vorm. Pott, G.m.b.H. (Müller⁶¹) states that emulsifiers may be made from condensation products of quaternary ammonium bases. For example, 100 parts of trimethylnaphthyl ammonium methylsulfate (naphthylamine treated with dimethylsulfate) are heated with 100 parts of isopropyl alcohol in the presence of 300 parts of concentrated sulfuric acid at 100°. The isopropyltrimethylnaphthyl ammonium hydroxide is soluble in water. The I. G. Farbenindustrie

A.-G. (Luther ²⁵⁶) prepares sulfonation products from the unsaponifiable portion of the oxidation products of paraffin, which consist especially of a mixture of alcohols with 10-25 carbon atoms, and mixes it with 33 per cent of oleum, the proportion used being calculated according to the weight of the initial alcohol at 35°. The oil obtained has emulsifying properties. Conversion of aliphatic or condensation systems of not more than 3 rings and containing aliphatic carboxyl acids with organic sulfo-amino acids, in which the SO₃H group is linked to a carbon atom of an aliphatic or heterocyclic group, results in the formation of an emulsifier.²⁵¹

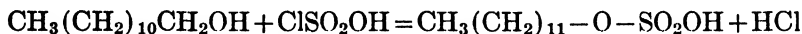
The I. G. Farbenindustrie A.-G.²⁵⁵ proposed preparing emulsifiers from sulfo-acetic acid esterified in the carboxyl group with tetradecylalcohol or dodecylalcohol. The Chemische Fabrik vorm. Sandoz ^{63,68} esterify a mixture of cocoanut oil and glycerin monoxylenyl ether, sulfonate it at the same time by treating with monohydrated sulfuric acid at 30-35° and neutralize the sulfonation product, which is a transparent, water-soluble oil, in preparing an emulsifier with good wetting ability. The I. G. Farbenindustrie A.-G.²¹² considers as a good emulsifier a compound corresponding to the general formula:



in which R₁ is any organic group; R₂, an alkyl group, and X, an organic group, or hydrogen.

The H. Th. Böhm A.-G.¹⁷⁰ propose an emulsifier obtained by treating high molecular weight aliphatic alcohols with sulfonating or phosphatizing agents in the presence of boric acid. For example, 30 kg of boric acid are stirred into 270 kg of a mixture of cetyl alcohol (iodine number 80); the mixture is gradually heated to 140°, and the resulting boric acid ester is sulfonated with 100-per cent sulfuric acid.

American Hyalsol Corporation (Bertsch ¹¹) use as emulsifiers and foamers sulfuric acid esters of a mixture of primary lauryl and myristyl alcohols (obtained from cocoanut and palm-kernel oils by esterifying their fatty acids with ethyl alcohol, reduction of the ethyl ester, distillation of the product, and collection of the first 50-60 per cent of the distillate). The higher alcohols are sulfonated to form alkyl sulfuric acids and neutralized to form water-soluble salts of the alkyl sulfuric acids. The reaction is as follows:



For example, 100 kg of a mixture of the fatty alcohols are heated to melting temperature, about 30°, and sulfonated at this temperature with 50 kg of chlorosulfonic acid.

Sulfonation may also be performed with fuming sulfuric acid at 100°. Oranienburger Chemische Fabrik A.-G.³⁴¹ claim as an emulsifier one consisting of a sulfonic acid, or its salts, of aromatic or hydroaromatic hydrocarbons replaced in the nucleus by sulfo groups, and containing

alkyl groups of at least 10 carbon atoms. For example, one mol alcohol, one mol toluene and 2.2 mols chloresulfonic acid yield at 25° sulfo-octadecyl toluene monosulfonic acid.

Fresinski and Heusler¹³⁰ prepare emulsifiers and foaming agents from salts of naphthenic or mineral sulfonic acids insoluble in water; the latter are mixed by heating with glue or gelatin. Henkel and Co., G.m.b.H.,¹⁶⁰ state that sulfonation of tertiary alcohols containing high molecular weight aliphatic groups with at least 8 carbon atoms is carried out in two phases, in which the alcohol is first treated with dehydrating agents, such as organic or inorganic anhydrides (sulfur trioxide or acetic anhydride), and then with a mixture of a sulfonating and dehydrating agent (acetyl or phosphorus chloride), from which emulsifiers are obtained. Aliphatic hydroxy-sulfides, obtained by the interaction of alkyl mercaptans ($C_{10}-C_{30}$) with halogen hydrines converted into their sulfuric esters by hydroxy-sulfide with an addition product of sulfur trioxide and a tertiary amine, may serve as emulsifying agents. Chwala and Waldmann⁷⁶ produce oil emulsions, using as emulsifying agents a mixture composed of neutralized and sulfurized animal or mineral oils, together with compounds having at least three double bonds in the constituent and combined with soaps of unsaturated fatty acids.

Waldmann and Chwala⁴²⁶ patented emulsifiers and foamers consisting of sulfuric acid or phosphoric acid salts of ethers with an amino or an alcoholic hydroxyl group, the latter containing higher fatty acids or resin acid groups. Sulfuric acid or phosphoric acid esters or sulfonic acids or their salts serve the same purpose.

Pilat³⁵² patented an emulsifier for preparing an 80 per cent thick emulsion of benzene in water. This emulsifier consists of sulfonic acids, or their salts, of hydrocarbons obtained from crude petroleum, to which is added protective colloids and a very finely divided inorganic substance. For example, 4.5 kg of a sodium salt of a mineral sulfonic acid are dissolved in 75 kg of water and added to a solution containing 7.5 kg of glue in 50 kg of water; a suspension of 0.75 kg of aluminum in 3 kg of water is also added.

The Standard Oil Development Co.^{402,403} brings about emulsification of mineral oils by using as emulsifiers oil-soluble sulfonates obtained by sulfonating highly refined petroleum hydrocarbons mixed with a hydroxylamine, triethanolamine, $N(C_2H_4OH)_3$, or salts of carboxylic acids containing more than 6 carbon atoms (oleic acid), together with a homogenizer, such as a polyhydric alcohol.

du Pont (Lehner and Mentzer¹¹⁰), in preparing a clear, stable anti-foaming emulsion, uses as an emulsifier a poly-alkyl naphthalenesulfonic acid or a water-soluble salt thereof. This emulsifier consists of 10-40 per cent of an alkali hydroxide or a carbonate, 0.5-3.0 per cent of alkyl amines, 1-5 per cent of a water-soluble salt of a higher fatty acid or, preferably, 5-20 per cent of a sulfonated acid or oil, and a high-boiling (150-250°) alcoholic residue, from a carbon monoxide-hydrogen catalytic synthesis, whose density is less than one, and in an amount equiva-

lent to or double the weight of the alkali, but less than 90 per cent of the emulsion.

Flett¹²⁴ claims as an emulsifying agent one prepared by boiling for about 16 hours a long-chain alcohol, such as commercial cetyl, lauryl, or palmityl alcohol, cetene, $\Delta\alpha$ -heptadecene, and a crude olefin (b.p. 237-262°) with phenol or pure or mixed cresols and zinc chloride or aluminum chloride and sulfonating the main fraction (boiling in the range 20°) of the resulting product.

As an emulsifying agent for use with liquid or solid substances, such as fats, waxes, hydrocarbons, oils, etc., insoluble in water, a mixture of benzyl alcohol and dissolved alkylated aromatic sulfonic acids or their salts is recommended.⁶⁰ Thus, butyl-naphthalenesulfonic acid is dissolved in water and added to benzyl alcohol to form an emulsifying agent for solvent naphtha. The I. G. Farbenindustrie A.-G. (Marx and Brodersen²⁴⁸) prepare an emulsifying agent from hydrocarbon oils obtained from brown-coal tar mixed with at least 50 per cent of aromatic or hydroaromatic hydrocarbons and then sulfonated in the presence of a small proportion (3-5 per cent) of methyl alcohol.

Oils and Prepared Emulsions

The addition of oils and prepared emulsions may also promote emulsification. This idea has been brought out in a number of patents. Billingham³⁵ prepares tar emulsions by using concentrated emulsifiers composed of substances previously prepared from a resin soap and a soluble protein. Braun and Hay⁴⁴ state that emulsions with a dilute alkali solution as the continuous phase are prepared by using as an emulsifier a small amount of an emulsion previously prepared. Morrell³¹⁵ converts an emulsion of a viscous liquid into one of a less viscous liquid by adding an emulsion containing as the internal phase a liquid less viscous than the initial emulsifying liquid. On the other hand, an emulsion of a readily flowing liquid may be changed into an emulsion of a more viscous nature by the addition of an emulsion containing as the internal phase a liquid more viscous than the substance emulsified in the initial emulsion. Certain relative proportions exist between the emulsion with the fluid oil and that with the more viscous emulsion. For example, if it is desired to produce a more fluid emulsion from an emulsion of a very viscous asphalt, an emulsion of a coal-tar oil, such as creosote oil, may be added to the latter. The globules of the coal-tar oil which are in the internal phase of the diluting emulsion will dissolve or disperse the globules of the viscous asphaltic substance, and an emulsion of a substance intermediate in character with regard to fluidity will be formed. Oils of a different nature (of vegetable or mineral derivation) combined in emulsions may be mixed in order to impart the characteristics of one emulsion to that of another.

Bouteille⁴¹ claims that emulsions can be produced when one or more secondary colloidal emulsions are introduced into the main emulsion, provided they do not enter into any reaction with it. A colloidal carbon

emulsion obtained by the decomposition of organic substances with sulfuric acid and phosphoric acid is mentioned as an example.

Basset and Szidon²² use tallow as an emulsifier for tar, asphalt and mineral oil. The mixture is mixed intimately in a colloid mill with an aqueous solution containing enough sodium hydroxide to saponify the tallow and a small amount of vegetable slime. Poolman³⁵⁶ prepares emulsions of about equal parts coal-tar oil and molasses in the cold with stirring.

Dogadkin and Lawrenenko¹⁰⁴ use as an emulsifier the waste product obtained by refining whale oil treated with sodium hydroxide or ferments. To 0.9 g of the waste product is added 1 cc of a 2-per cent sodium hydroxide solution; this serves to emulsify 15 cc of benzene in 10 cc of water.

Parkhomenko^{344,345} describes a new method of preparing oil emulsions. The alkali sludge obtained after adding sodium hydroxide to the sulfuric acid-treated transformer, spindle, or turbine oils is 'salted out' with sodium hydroxide (35-40° Bé.) (sodium chloride should not be used if corrosion is to be avoided), and the upper layer used in the preparation of the emulsion either directly, or after adding the required proportion of oil (10-100 per cent). The mixing of the components is carried out at 60-70°.

Emulsification Processes

Perry and Bullock³⁴⁷ allow oil in known proportions to flow into a stream of water maintained under pressure. The flow of the oil is regulated by the admission of air and the resulting emulsion is delivered to a point of discharge. Kuczynsky²⁹¹ prepares emulsions without protective colloids by an electric dispersion method in which the conductive phase is led through small openings into the dielectric phase. It is assumed that the emulsion formed changes the chemical composition of the petroleum oil emulsified by a polymerization process.

Wood and Loomis,^{436,437} Richards and Loomis,^{370,371} Freedman¹²⁸ and Richards³⁶⁹ proposed the use of ultrasonic waves of very high frequency of the order of 200-500 kilocycles per second. Many different emulsions were obtained by irradiating pairs of immiscible liquids with these sound waves.

deCew⁸⁹ forces the substance to be emulsified and the hot soap solution from opposite directions, through a perforated screen in fine streams, meeting preferably at an angle of 180°. This contact causes violent agitation, coupled with breaking up of the liquids into fine streams as they are forced through the minute openings, and produces an excellent atomizing effect, which results in emulsification. For some substances, it may be necessary to force the liquids through a second screen, or a similar device, regulating the pressure accordingly.

Boleg³⁸ recommends treating an oil-in-water mixture with air in a pressure apparatus. The mixture is subjected to a pressure of 1.0-1.5 atmospheres and superheated by vapor acting indirectly. Oils containing

50 to 75 parts of condensed water are mixed with compressed air at increasing temperature up to 125°, with or without gelatin or glue, the water evaporated being renewed continuously until a transparent emulsion is formed.

Alsberg⁹ places the oil to be emulsified in a mixer containing a gum and glycerin solution; the substances are then agitated in the cold until the ingredients are thoroughly incorporated, and the mixture led into a homogenizer equipped with a discharge valve regulated for 3500 to 4000 lbs/sq in, thus insuring the formation of oil globules of substantially uniform size. This method is recommended for the preparation of stable emulsions of uniform particle size.

Holmes and Williams^{107a} propose rotating rapidly, in a suitable container, a definite volume of a fatty liquid containing impurities, withdrawing the mixture from the container by the momentum of the liquid induced by the rotation, and developing pressure in the liquid by obstructing its flow. The fatty mixture is broken up into globules or emulsified in the aqueous phase by passing it in the form of a thin film at high speed between two adjacent surfaces.

The Petroleum Sand Products Corporation³⁴⁸ heats heavy oil to its temperature of vaporization. The vapor and oil, while being heated to a cracking temperature, are emulsified by means of an agitator rotating at a speed of 400 to 600 r.p.m. A vapor-oil emulsion is obtained. Polanyi and Bogdandy³⁵⁵ prepare colloidal metal emulsions by evaporating or volatilizing the constituents of insoluble substances by cathodic atomization.

For the continuous preparation of liquid and gas emulsions, particularly in the case of heavy oil dispersions for oil burners, Auger¹⁵ recommends combining the liquid and the gas under the same pressure by means of a porous ceramic body, the gas passing from the latter being dispersed in the streaming liquid. The Kraft-Phenix Cheese Corp. (Chapman²⁸⁵) effects continuous emulsification by intimately mixing the substance to be emulsified with the emulsifier in definite proportions and adding, during the emulsification process, a measured amount of a suitable gas, and at the end of the reaction, an addition substance.

The Lancaster Processes, Inc. (Robinson²⁹⁴) produce emulsions by dividing the streaming material to be emulsified and dispersing these streams in a previously prepared circulating emulsion. The latter stream is preferably divided, the material to be emulsified being added to one portion, and water and the emulsifying agent to the other portion, after which the two portions are recombined.

The Submarine Signal Co., Ltd. (London)⁴⁰⁸ produces emulsions from liquid mixtures by passing them between two parallel surfaces spaced 0.25 mm apart, one of which is subjected to electromagnetic vibrations. The frequency of these vibrations is so adjusted that resonance is set up in the liquid mixture. A frequency of 4000 vibrations is preferred.

Schutte^{388d} effects commercial de-oiling of waxes, containing high

end-point constituents which render them unsweatable, by emulsifying the oily wax in a non-viscous, non-solvent liquid, such as water. The process is controlled so that water becomes the continuous phase of the emulsion and the droplets of oil and the wax crystals are separated by water; a freely filtering substance is obtained. An improvement in crystal structure is claimed to be due to the fact that the wax is solidified from a thin interfacial film, rather than from the main body of the liquid. The cooling and emulsification are carried out in the same zone by the addition of the non-solvent liquid at a suitable temperature.

Types of Equipment Suitable for Use in Emulsification

Colloid Mill

There are many variations in the methods for producing emulsions and consequently various types of devices. Some of these are based on a beating action, others on a stirring mechanism. Grinding is the principal action of the colloid mill, which owes its popularity to the fact that it produces a finely divided system. As suggested by Travis,⁴¹⁷ the term "dispersion mill" is more applicable than "colloid mill." When applied to emulsions, the colloid mill is a dispersing mechanism rather than a fine-grinding device. The colloid mill is a device made up of two surfaces rotating one upon the other, between which pass the materials to be emulsified. A colloid mill may also consist of a series of channels in which two grinding surfaces are fitted. Credit for the actual construction of the first colloid mill should be given to von Weimarn,^{422,423} but Plauson³⁵³ obtained the first patent granted on this device. Colloid mills, classified according to their mechanism, may be divided into three groups: (1) beater type; (2) smooth-surface type; and (3) rough-surface type.

Types. (1) The *beater type* colloid mill includes the original Plauson mechanism and its modifications. In this mill the particles to be divided are subjected not only to hydraulic shearing stresses, but also to impact stresses produced by revolving blades entering and leaving the spaces between the fixed blades. It is claimed that the Adesberg and Auspitzer¹ mill is an improvement over the Plauson device because the power requirement is decreased to one-seventh of that of the original Plauson mill of equal capacity.

(2) The *smooth-surface type* depends for its operation on hydraulic shearing stresses. Machines of this type consist of a smooth rotating surface passing over a smooth stationary surface at a velocity of 2 miles or more per minute, and with a minimum clearance of 0.001 inch. The speed with which the rotor moves varies from 1,000 to 20,000 r.p.m. By the adsorption of fluid films, tremendous shearing stresses are forced upon the working surface. These stresses are responsible for the division of the material.

(3) The *centrifugal smooth-surface type* has as its working surface either a truncated cone rotating within a fixed cone, or flat discs rotating

in opposite directions. The delayed-action smooth-surface mill has a cylindrical working surface which is mounted on a horizontal shaft. The peripheral speed varies slightly over the working surface so that the material treated tends to remain between these surfaces for a long time. In this device, the material is fed to the working surface through channels in the rotor.

(4) The *rough-surface type* employs a rough working surface which, in addition to the hydraulic shearing stresses, has a second dividing action involving an intense turbulence and a beating produced by the currents in the liquid between the irregular surfaces. Otherwise, this type of mill is similar to the centrifugal smooth-surface type with truncated cone or flat discs.

The turbine type embodies features of both the smooth- and the rough-surface colloid mill, with the advantage of an intensive and prolonged dividing action.

Kinds. Among the colloid mills are: 1. Premier; 2. Hurrell; 3. Charlotte and 4. Rex.^{57, 75, 136, 147, 158, 312, 319, 320, 354, 377}

(1) The *Premier* mill has an outer casing surrounding a rotor which is a smooth metal cone working in proximity to a fixed conical seat. The clearance between rotor and stator is 0.001 inch or more. The rotor has a speed varying between 5,000 and 25,000 r.p.m. When feeding the mill by gravity, the rotor acts as a centrifugal pump drawing the emulsion between the working surface, and while it is passing as a thin film through the narrow space between the conical surfaces, it is subjected to an intense shearing action.

(2) The working surface of the *Hurrell* mill constitutes the bore of the cylindrical body. Two circular covers equipped with a gland through which the rotor shaft passes are bolted to the stator. The bearings with frames are housed on extended arms, each bearing being carried within a bronze sleeve sliding in the bracket arm to which is attached a micrometer screw fitted with a large handwheel. Each half-turn of the handwheel alters the clearance by 0.001 inch, and the rotation of the wheel adjusts the thickness of the film. The shearing forces exerted on the emulsion originate between the fixed and the rotating parts. The tendency of the emulsion in the gap to leave the space due to its own inertia is prevented because of the cylindrical form of the rotor. The displacement is effected only by a ring of emulsion of varying radial depth in the space between the halves of the rotor. The emulsion formed is discharged from two outlets, one located at the bottom of each cover. Since the emulsifying space is practically parallel with the axis of the rotor, there is no centrifugal force causing the displacement of the emulsion; consequently, the time during which emulsification is effected depends only on the rate of feed.

(3) The oil in the *Charlotte* mill is fed by gravity and forced into the gap between the conical rotor and the conical stator against the action of centrifugal force which tends to retain the emulsified material. The rotor and stator are grooved differently than in the smooth surface type

mill, the grooves being radial, the currents set up in them giving rise to an intense beating and chopping action. Thus, in addition to shearing forces, this device produces in its grooves whirling currents which have an intensive beating effect.

(4) The *Rex* mill is a rough-surface type with intercalating pin discs. A horizontal rotating disc is provided with studs and runs placed co-axially against a superimposed stator disc also provided with studs or short thick pins, the pins of each disc overlapping in such a manner that the material emulsified passes out radially and strikes the pins in both discs. The emulsion enters through a hopper in the center of the stator disc, the discharge taking place at the circumference where the distance between the discs is the least.

In order to obtain a more uniform dispersion of prepared emulsions, a so-called homogenizer is used. The difference between a homogenizer and a colloid mill is not in the principle of operation, for both mechanisms depend for their dividing action mainly on the hydraulic shearing forces exerted upon the particles suspended in the fluid medium and may operate under high pressure; but they differ with respect to the ultimate end in view. The simple type of Briggs' homogenizer^{46,47} for laboratory use consists of a reservoir containing the emulsion, which is withdrawn through a trap opening by means of a suction pump, passes out through very small openings in the orifice, and strikes a baffle plate. Homogenization may be effected under high pressure of many thousand pounds; but a high-pressure homogenizer operated at 2000-3000 lbs/sq in is not suitable for the dispersion of solids or for the homogenization of heavy liquids.

Mixing Equipment

Bullock's patent⁵² relates to the emulsification of suitable components in an apparatus designed for the mixing of oils of varying composition with water. Regulating the flow of the oil to the injector, as well as the quantity of oil in the emulsion, which should be proportional to the amount of air admitted, is a new feature of this device.

Fish¹²³ employed for emulsification an apparatus comprising a multi-cylinder pump consisting of a number of graduated as well as compression cylinders, a valve mechanism, a mixing device, and a discharge valve. The feed or delivery of liquids to the pump is automatically regulated. The liquids to be emulsified are measured, mixed and impregnated with an expansible fluid or gas and the resulting mixture subjected to a high pressure. Finally, the mixture is released into a chamber maintained under a comparatively low pressure.

Schroeder's patent^{387,388} deals with the preparation of emulsions in a series of mixing containers connected by narrow tubes. The mixing containers are jacketed and each is provided with an agitator. The rate of rotation of these agitators decreases gradually, from the first container to the last of the series. The mixing containers are arranged stepwise, that is, one above the other, which causes a continuous flow of emulsion com-

ponents from the top container, the emulsified material being drawn off from the bottom.

Alexander's invention⁷ refers to a centrifugal machine for the intermittent mixing of liquids. This apparatus has a novel form of bearing for the spindle of the mixing bowl which permits the proper operation of the spindle and makes it adjustable. An apparatus comprising a chamber provided with a central shaft around which a number of rotating mixing screws revolve is described in the literature.⁶ The blades of the mixing screws are perforated and rotate clockwise and counter-clockwise on alternate screws. The outer edges of the blades of the screws come in direct contact with each other, as well as with the wall of the chamber.

Kirschbraun²⁷⁵ describes a mixing apparatus for the preparation of emulsions of bitumen, clays, etc. and water. The speed mixer type²⁸⁰ consists of two propellers which are adjustable to different heights on the shaft. By reversing the pitch of the lower propeller, a powerful upward pull from the bottom of the mixing container is produced, while the upper propeller produces a downward pull. The two opposing forces are pitched against each other between the two propellers and the liquid is thrown with force against the sides of the container. The emulsion is thus violently agitated. Mixing containers equipped with different types of stirring devices are available. One type comprises a rotating cylinder²⁷⁹ fitted with a hollow truncheon carrying a horizontal revolving shaft, having a number of beaters arranged to run in a direction opposite to that of the cylinder and its contents. Although mixing containers or tanks are designed, as a rule, for individual batches, yet they may be used for bulk batches as well; this has one great advantage, *i.e.*, it permits the total volume of the continuous medium to be present at one time before introducing the phase to be dispersed by agitation, thus producing a uniform, homogeneous mass.

McFadden³⁰⁷ patented a unit apparatus in which all the movable parts are driven from a single shaft. This apparatus consists of a tank for mixing the materials, dissolving the emulsifier by heat and emulsifying the resulting mixture. In addition, this device is equipped with a cooler in which the emulsion is chilled. The section in which emulsification is effected consists of a rotating bowl, and the cooling element is cooled by brine circulated by a rotary pump.

Thiberge⁴¹² proposed a method for continuous mixing or emulsifying of viscous liquids, such as lubricating oils, by pouring the liquids in the form of thin layers or threads into a stirring equipment at various points. Hildebrandt's device¹⁰⁴ for mixing and emulsifying consists of a closed space in which a rotating plate with a permanent hood attachment is arranged, the substances to be emulsified whirling around and underneath. The Gas Light and Coke Co. (Murdoch and Shannon¹⁴⁰) mixes the emulsifying components in a liquid state and forces them repeatedly through nozzles toward surfaces arranged a short distance from the bottom of the receiver. Continuous, as well as intermittent, operation is possible. Emulsification may be effected by using evaporating or steam-

ing equipment.⁸⁸ The heating surface³²² of an evaporator provided with double walls assumes a concentric form terminating in a funnel-like shape which originates in the liquid as a result of stirring. The sloping anchor-form stirring paddle rotates a short distance from the heating surface. The temperature of the emulsified liquid is uniform throughout the whole mass, and no foam formation accompanies the evaporation.

High-pressure Apparatus

In this type of apparatus the material to be emulsified is forced or squeezed under pressure through a homogenizing valve at a velocity which breaks up the substance into globules to an extent sufficient to homogenize the product.

Hurrell's apparatus¹⁸¹ is of the pressure type and is commercially known as the Gaulin. High-pressure pumps force the mixture of oil and water between a conical valve and a seat similar in shape, above which the valve is held by means of a spring, causing the formation of an emulsion.¹⁸² According to a patent issued to the Chemische Fabrik vorm. Griesheim-Electron,⁵⁰ the liquids pass under pressure through nozzles to a centrifugal wheel. A hydrostatic or gas pressure is used for this purpose. The greater portion of the liquid entering the case of the mixing apparatus is continuously removed by means of a suction pump which takes off the liquid at the external circumference. The discharge of the case takes place by running off the liquid brought from the centrifugal wheel to an outlet tangentially located.

Browner⁵¹ constructed an apparatus providing means for compressing several components and squeezing or forcing the oil under pressure and at high velocity. The substance is thus broken up into globules to such an extent as to homogenize the resulting product.

deLaval⁹² prepares emulsions by forcing the liquid fat or oil in fine streams through minute openings under high pressure into liquids kept under low pressure. The apparatus consists essentially of two reservoirs and a force pump, the outlet of which is controlled by a heavily loaded valve adjusted by a fine screw. (See drawings in patent.)

Walsh⁴²⁷ patented an apparatus for the emulsification of oils in water by pressure obtained by piston strokes.

Emulsification may also be carried out by spraying the substance to be emulsified by means of compressed gas, air, steam, high pressure, and the like, whereby the atomized substance is incorporated in the dispersion medium used.^{3,4} The atomizing device, preferably an annular disc, is submerged below the level of the dispersion medium. With suitable provision for the feeding of the material to be emulsified and the drawing off of the emulsion obtained, the process is made continuous.

Empson,¹¹⁵ as well as Stewart, Riesen and Hargreaves,⁴⁰⁶ patented an apparatus for emulsification. Schrader and Stahl³⁸⁵ constructed an apparatus for the preparation of emulsions which consists of a perforated plate moving backward and forward in a cylinder through which material is forced and emulsified in a relatively short time. However, before emulsi-

fication can take place, the air must be pumped out of the apparatus and a vacuum maintained. Frazer and Walsh¹²⁷ describe an apparatus for preparing finely divided oil-in-water emulsions with particles 0.5 mm in diameter or even smaller. Gropengiessen¹⁴⁸ prepares emulsions in a narrow tube in which the dispersion medium flows under pressure. In counter-current flow, the disperse phase is introduced through narrow tubes under regulated pressure. A violent bombardment of particles of both phases against one another in the narrow tube results in good mixing.

Hurrell¹⁸⁰ describes a pressure apparatus for emulsification, provided with a pump between a cylinder and flasks with numerous narrow openings through which the mixture to be emulsified is forced. The flasks may also be provided with narrow, screw-like drilled holes through which the mixture flows at high velocity. Cremac Marketing Co., Ltd. (Richards, L. S., and Richards, E. M.⁸⁵) carry out emulsification in a pump cylinder. By drawing back the piston, a part of the mixture is sucked in and forced out by pushing forward through a threaded opening. The outlet is kept so small that it acts as a back-pressure orifice. Pushaj^{359, 360} describes the "impulsor emulsifying apparatus" as an example of progress in the technique of emulsion preparation. This emulsifying apparatus operates with a rapid change in pressure followed by intensive stirring. Mangrove³⁰³ uses in his preparation of emulsions an arrangement consisting of a cylinder in which an adjustable block, with a rough bottom, is placed. According to N. V. Handel-Maatschappij "Delma,"³³³ the liquids to be emulsified are forced through channels in such a way that they come into contact with opposite streams within the channels and flow out perpendicularly to them.

The Gas Fuel Corporation (Russell^{138, 139}) prepares a substantially permanent emulsion by thoroughly beating together an aqueous liquid, a heavy liquid hydrocarbon and a gas under superatmospheric pressure. In another patent¹³⁷ is related the production of oil-gas from an emulsified mixture of this character by admixing the mixture with a highly heated gas and spraying it into a hot zone heated at a temperature sufficiently high to form a permanent gas.

Application of Centrifugal Force

Paul, Allen and Rosengren³⁴⁶ force liquids to be emulsified through a device operating on centrifugal force and pass two or more liquids to be emulsified through narrow spiral passages formed in a centrifugal head. For this purpose, the device is rotated at a high rate of speed by means of a steam turbine directly connected with it. Brewer⁴⁵ makes use of a centrifugal power machine for the production of emulsions of fatty substances.

Povey³⁵⁷ describes machines for disintegrating or emulsifying materials. The substances to be emulsified are driven by centrifugal force through zig-zag clearance spaces between rings of oppositely rotating and intermeshing blades. Alexander's arrangement⁷ for emulsification makes

use of superimposed horizontal plates fitted in a centrifugal drum and so arranged that alternate plates reach up to and around the periphery of the drum, the intermediate plates with openings at their centers being fixed to the outer wall. The liquid travels in one direction upon one plate, and in a reverse direction upon the other plate. One of the plates is constructed to permit the passage of material downward near its periphery. Another of the plates is so constructed that material is permitted to pass downward near its center. After passing through the plates the liquids are thoroughly mixed. Means are provided for rotating the drum. The liquid flowing from the drum is collected in a casing which encloses the apparatus.

Empson's apparatus ¹¹⁴ comprises a centrifugal rotor with narrow passages through which the mixture passes. The outlets from the rotor are much smaller than the passages. These passages are kept filled with the mixture and the size of the outlets is varied by changing the screws or by some similar means. A collecting case is provided for the excess feed, as well as for the emulsion formed. In the latter case vanes are used for arresting the motion of the emulsion and aerating it. The aeration is controlled by varying the amount of air drawn into the emulsion casing.

Nyrop's patent ³³⁴ deals with emulsification in a centrifugal apparatus comprising a pair of rotating horizontal discs with the space between them filled with solid materials, such as glass, wool, wire, netting, or granulated pumice. The material to be emulsified is fed into a space at the center of the discs, which is left free from solid materials, and discharged in an emulsified state at the periphery. Besides the materials forming the final product, other gases or vapors, or hot gases for drying, may be introduced. The material used for filling may also have catalytic properties, producing a chemical reaction.

Ferns, Stapley and Harrison ¹²⁰ feed materials to be emulsified into a hollow vertical shaft on which are mounted a number of metal discs forming narrow annular spaces and provided with thick, adjustable rims, the materials entering the spaces between the discs through holes in the shaft. The emulsion formed is thrown out through the narrow openings by centrifugal force. The emulsification apparatus of Westenholz and Nyrop ⁴²⁹ is a casing divided by a partition into two compartments, in one of which rotating vanes turn on a horizontal axis. The vanes are perforated and the liquid is forced through the perforations by means of radial projections attached to the casing and directed inward. The liquid to be emulsified enters the casing near the center and leaves the centrifugal compartment through holes near the periphery of the partition, passing through the second compartment to a central outlet.

Ramesohl and Schmidt ³⁶³ describe an emulsifying arrangement connected with a centrifuge operated by friction discs which divert the flow of liquids in such a manner that the upper disc is displaced longitudinally to one or more laterally arranged taps or pegs running parallel to the rotating axis. Such an arrangement is suitable for use in a centrifuge,

but the space over the friction discs is not subject to displacement and may therefore be used to divert the direction of flow.

Vredenburg (Bendixen ^{424, 425}) suggests emulsifying in a mixing drum in which two concentrically-bound plates are located. The material is introduced in a swirling motion and brought into rotation by centrifugal force. The emulsion is withdrawn through a screen in an opening arranged at the bottom of the container. Dussek Bitumen Company, Ltd. (Hatt ¹¹³) emulsifies and homogenizes in a cylindrical chamber running parabolically upward and provided with a stirrer forcing the mixture toward the chamber wall, where it is spread out in a thin film and emulsified under the influence of centrifugal force. The mixture introduced into the chamber in a swirling motion is discharged tangentially as an emulsion. Hurrell ¹⁷⁹ centrifuges substances to be emulsified and forces them through a special slit in such a manner that the emulsified substances leave the apparatus under pressure, but without foam formation. The slit is formed by the peripheral surface of a rotating wheel and the ring surface forming a part of the case surrounding the wheel.

Müller ³¹⁷ emulsifies substances by subjecting them to centrifugal force under pressure and forcing them through fine-mesh wire screening.

Stirring Equipment

Bahm (Hamburg ¹⁷) states that rapid and intimate emulsification may be effected by agitating the mixture of oil with two concentric right- and left-hand worm gears. The inner edge of the inner worm gear extends nearly to the driving shaft, and the outer edge of the outer worm gear almost touches the wall of the chamber. A heating coil surrounds the worm gears for the greater part of their circumference. Blores' apparatus ³⁶ comprises a cylindrical receptacle fitted with a cover and a perforated dasher within the receptacle. The spindle of the dasher passes through a packing gland in the cover and is fitted with an operating handle. The cylinder may be made of cast iron and fitted with a tinned or enameled lining. The dasher is dome-shaped to increase its efficiency. Suitable provisions are made for filling and emptying the receptacle.

The Colloidal Equipment Corporation (Cunniff ⁷⁹) patented an apparatus comprising a pair of discs, with intercalating ridges forming a zig-zag passage, rotating in close proximity with varying speeds. The inlet admitting materials to be emulsified is axial, and the outlet for the emulsion is at the periphery. One of the discs is provided with a deep flange which embraces the other disc and causes the final outlet to be comparatively near the axis. Povey and Hallas ³⁵⁸ constructed an apparatus in which the materials to be emulsified are delivered axially in opposing streams impinging within coaxial members rotating in opposite directions. The adjacent faces are provided with intermeshing blades and the materials passed through the device are discharged through a narrow annular duct into an annular collecting channel surrounding the rotating members. The device is particularly applicable for the emulsification of two or more liquids.

The apparatus of J. Harrison-Carter, Ltd. (May and Barradell ²⁸⁷) has a pair of discs, one of which is rotated at high speed. The discs are provided with concentric intercalating rings or teeth, triangular in shape. Each disc has a number of grooves running from the center to the periphery. The clearance between the discs ranges from 1/1000 to 3/100 of an inch. McGongan and Hunter ³⁰⁸ patented an apparatus comprising a chamber containing two interacting grooved rollers, which serve as emulsifying devices, and a feed hopper connected with the emulsifying chamber by a pipe. The discharge pipe from the latter has an auxiliary branch by means of which the emulsion may be returned to the hopper and back again to the chamber for re-emulsification, if desired.

Schroeder's apparatus ^{387,388} for the preparation of emulsions consists of a rapidly rotating shaft carrying a block which has an annular rotating grinding surface bearing toward an annular fixed grinding surface. In the clearance between the two grinding surfaces is located a turbine which is fixed to the rotating block. The liquid to be emulsified enters the turbine and is forced under high pressure between the two surfaces from which the emulsion obtained is drawn off. Whatmough's patent ⁴³¹ refers to an apparatus for the production of dispersions of amorphous aggregates in liquids. The apparatus consists essentially of a liquid-tight casing within which is a rotor provided with one or more reticulated beater arrangements which can be rotated at high speed. Baffles, similar in structure to the beaters, are employed to direct the liquids into the path of the beaters. The beaters are constructed wholly or in part of wire gauze which subjects the amorphous aggregate to a rubbing action, whereby the material to be emulsified is effectively dispersed throughout the liquid. If the rubbing action is confined to the surface of the wire gauze, maximum efficiency is obtained only by repeated treatment or by allowing the solid particles, while suspended in the liquid, to impinge at high speed on the beaters, through the interstices of which the liquid passes when subjected to friction.

Fette ¹²¹ patented an apparatus consisting of a chamber with a central shaft around which a number of rotating mixing screws revolve. The blades of the mixing screws are perforated and located on alternate screws in right- and left-hand directions. The outer edges of the screw blades come into direct contact, on the one hand, with each other, and on the other hand with the wall of the reaction chamber. In Butler's apparatus ⁵⁴ the emulsification chamber has one fixed and one rotating wall on each of which are located annular projections forming recesses inclined in opposite directions on opposite walls.

The deLaval Separator Co. (Hapgood ⁹³) constructed an apparatus consisting of a chamber divided into a number of compartments by cross partitions, every one of which has a beveled orifice and a corresponding disc with beveled edge forming the emulsifying partition. The discs are mounted on a common driving-shaft. One of the compartments has at its end an outlet orifice for the completed emulsion, and the other compart-

ments have inlet orifices for the ingredients, which may be introduced in varying proportions at different stages.

Fig. 4 shows a typical installation of a deLaval emulsor on one side of which an emulsion tank is connected directly; on the other side, a mixing tank equipped with an agitator and a steam coil is indirectly connected. A centrifugal pump connects the emulsor with the mixing tank. Measured quantities of oil, water and alkali are fed into the mixing tank, heated and agitated until the ingredients are so mixed that the emulsor receives a uniform charge at all times. This mixture is led from the mixing tank into the emulsor by opening a valve on the pipe line connecting the two chambers through the centrifugal pump and is discharged from the emulsor into the emulsion tank. When this tank is full, the valve on the mixing tank is closed and the valve on the emulsion tank opened, which allows the liquid to be pumped into the overhead tank.⁹⁴

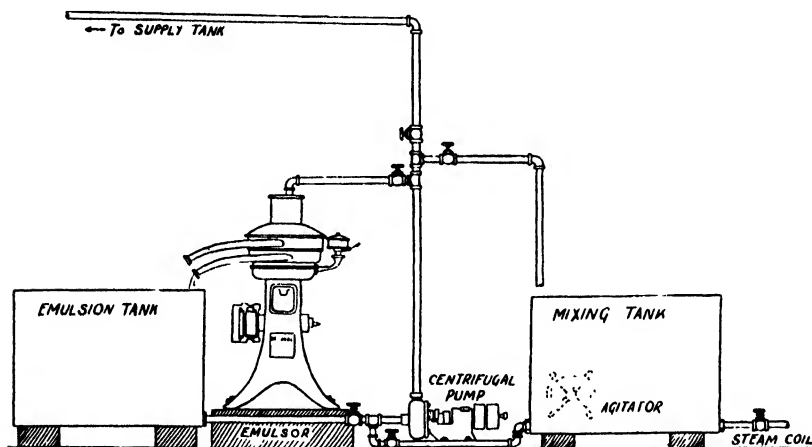


FIG. 4.

Seaman, Brinjes and Goodwin, Ltd.³⁸⁰ patented an apparatus the emulsifying mechanism of which is composed of two parts, one part being designed to rotate and coöperate with a stationary part, both parts being supported and retained in a container in which the mixing takes place. Both the rotatable and non-rotatable parts of the mechanism are supported by a rotatable spindle; the stationary part comprises a number of projections extending downward and carried by a spider, or a three-armed frame. The rotatable part of the emulsifying mechanism consists of a wedge-shaped member from which project in an upward direction several fingers or mixing knives designed to coöperate with the downward expending fingers or knives carried by the spider, the former being rigidly secured to the spindle and the latter loosely mounted on the spindle, which is provided with a collar at any desired distance below the spider frame so as to lift the frame when the spider is raised. The spider

frame can be readily lifted out of the container by means of a chain actuated by a motor and passing over a pulley.

The apparatus described by Hutchings¹⁸³ is a truncated hollow cone with ducts in the walls. These ducts extend from the base to the top, and are connected with the interior of the cone when it is rotated at high speed in the material to be emulsified. The liquid is drawn up into the interior of the cone and the emulsion formed passes out through the ducts. The vortex formed in the liquid causes the top of the cone to be always uncovered so that a certain amount of air is drawn in. If this is not desirable, the operation may be carried out in a vacuum. Steen⁴⁰⁴ refers to a shaft with stirring blades rotating in a container provided with heating coils at the bottom and with a finely perforated tray at the top. One of the constituents, *e.g.*, water, in the case of water-in-oil emulsions, is passed through the perforated tray in the form of mist. The stirring blades are inclined in one direction at one end of the shaft and in the opposite direction at the other end, and may be readily exchanged for others of varying pitch.

Allen and Haadbury, Ltd. (King⁸) state that emulsions may be prepared in a container having radial arms rotating in opposite directions. These arms have a number of blades arranged concentrically on either side, and the material passes between these blades to the other set of radial arms. Every blade resembles an equilateral triangle with two sides curved inward and one side outward. The apex of the blade indicates in which direction the radial arm moves. These blades give the liquid a whirlpool effect destroyed by the movement of the radial arms; thus efficient agitation is secured.

Sousthagen, Wood and Kanook Co., Ltd.³⁹⁷ subject materials to be emulsified to a combined oscillatory and translational motion, using beaters or vanes on a rotating shaft, alternate sets of vanes being of opposite inclination and of varying pitch. The ends of the vanes may be bent and shaped to overcome the radial motion of the material and at the same time to retain it within the sphere of activity of the beaters. Working the material in batches and passing it many times through the beaters is preferred.

Anode Rubber Co., Ltd. (Klein and Szegvari¹²) subject the components of a mixture to be emulsified to the action of hard, round grinding elements kept in motion by a stirrer. The mixture is circulated between the emulsifying device and a sedimentation or centrifugal separator in which the coarse, unemulsified particles are separated. The diameter of these grinding elements should be between 1 and 8 mm. Two sizes may be used, one size being at least twice the diameter of the other. The metallic parts of the apparatus may be covered with rubber and a cooling system is provided. The Altonaer Werke (Mohr and Co.¹⁰) claim that, in order to prevent the pressure exerted by the liquid to be emulsified from increasing the friction between the spindle and the bearings, the spindle should be driven by a pulley fixed at the middle and provided with a rotating friction disc at each end. These friction discs work in

conjunction with a fixed grinding surface, and have their blades curved in opposite directions so that the torsion of the liquid at each end tends to turn the spindle in the same direction, thus lessening the power required to drive it.

Werner ⁴²⁸ emulsifies two liquids of different specific gravities by withdrawing them from the bottom of a container in order to establish a vortex therein and thus to develop a flow of the upper and lower liquids together through the outlet. The stream of mixed liquids is directed against the smooth face of a rapidly revolving disc; in this way the lighter liquid (crude oil) is dispersed in the heavier liquid (brine) irrespective of their "natural" emulsification characteristics, and the mixture returns to the container in a tangential direction, developing a rotary motion and avoiding the vortex.

Steenberg ⁴⁰⁵ patented a churning and emulsifying machine comprising a cylindrical container in which is arranged a close fitting worm conveyor with single or multiple perforated threads and an adjustable valve placed at the discharge pipe. The machine operates in such a manner that the material is forced toward the discharge end, where it is compressed by the rotation of the worm. The worms used may have different holes and pitches, and by varying the speed of rotation of the worm and the setting of the discharge valve, diverse conditions are produced, whereby churning and emulsification can be varied. The cylindrical container may be kept at any desired temperature by means of a steam or water jacket mounted either horizontally or vertically.

The National Aniline & Chemical Co., Inc. (Zwilmeyer ³²¹) prepared emulsions with a mechanical stirrer or air pressure. The substances are emulsified with vapor through a dispergator, using protective colloids (dextrin or Turkey-red oil). The Flintkote Co. (Gregg ¹²⁶) leads the substance to be emulsified, the emulsifier and water continuously into a cylinder equipped with a stirrer, the emulsion formed circulating within the container. The Lancaster Processes, Inc. (Robinson ²⁹³) recommend introducing water and soap or clay in a continuous stream and circulating the components. At the same time, the substance to be emulsified is introduced into this stream in a liquid state, the emulsion formed being continuously discharged from the container. The Gas Fuel Corporation (Russell ¹³⁷) effects emulsification of crude petroleum or other heavy oils by introducing it into preheated water placed in the lower part of an emulsifying chamber, while a gaseous component, *e.g.*, air or carbon dioxide is introduced from above into the stirrer under pressure. The emulsion formed may be used directly as fuel.

The Sinclair Refining Co. (Shropshire ³⁹²) effects emulsification by using two series of radiating spokes rotated on separate shafts in opposite or relative directions. The rotors are enclosed in a casing suitable for resisting pressure, the inlet being axial and the outlet at an intermediate radius.

From the foregoing, it can be clearly seen that emulsification can be

carried out successfully when all factors influencing production are considered and the proper equipment selected.

Appendix

The distribution in United States production of crude petroleum by states reported in January, 1939, by the Department of the Interior * is as follows:

State	Thousands of Bbls.
Texas	484,527
California	224,354
Oklahoma	160,072
Illinois	94,302
Louisiana	93,869
Kansas	60,723
New Mexico	37,323
Michigan	22,799
Wyoming	21,417
Arkansas	21,143
Pennsylvania	17,337
Montana	5,961
Kentucky	5,581
New York	5,098
West Virginia	3,580
Ohio	3,156
Indiana	1,443
Colorado	1,391
Total United States	1,264,256

The total domestic runs to stills in 1939 has been estimated as 1,237,-840,000 barrels. Crude runs to stills for December, 1939, are as follows:

State and District	Thousands of Bbls.
Texas Gulf	27,241
Indiana, Illinois, Kentucky	17,848
California	16,669
East Coast	14,978
Oklahoma, Kansas, Missouri	9,312
Texas Inland	5,313
Appalachian	4,262
Louisiana Gulf	3,588
Arkansas and Louisiana Inland	2,199
Rocky Mountain	2,058
Total	103,468

Emulsions may form in any field where water is produced with oil, whether such water exists in the oil sand itself or enters the hole from strata above or below the producing sand. Water is present in virtually all producing fields in the United States.

The nature and the amount of emulsion formed vary for any particular field. In some producing fields the emulsion percentage is rather

* United States Department of the Interior, Bureau of Mines, Monthly Petroleum Statement No. 193.

small, in others large; Pennsylvania, West Virginia, southeastern Ohio and eastern Kentucky fields produce only small amounts of emulsion, which separates readily into oil and free water. The Lima district, Ohio and Illinois and western Kentucky fields produce more emulsions, and treating is imperative. All Kansas fields have a large percentage of emulsions and dehydration is of prime importance. In Oklahoma the percentage of cut oil produced is large, except in several light-oil districts. In Arkansas the emulsion problem is more serious than in almost any other locality. In Texas high percentages of a very poor cut oil are produced in the Gulf Coast region, and the percentage in north Texas light-oil fields is small.

The Mexia, Currie and Powell fields fall between the two extremes. In the Louisiana fields emulsion problems are much the same as in Texas and Oklahoma. In California more than 10 per cent of the yearly production is emulsified. The difficulty of handling these emulsions varies with the character of the crude. The heavy Casmalia oil forms an extremely stubborn emulsion, whereas certain light oils of the Los Angeles basin do not emulsify badly. In Wyoming and Montana, emulsion formation is not of such great concern as in some other states; the amount of water is not large and the yield is chiefly light oil. Of course, it is important to realize that as the fields grow older the emulsion problem changes and sometimes becomes more serious. Likewise, oil from the same wells often varies from one extreme to the other as operating conditions and atmospheric temperatures change. Conditions in wells flowing naturally or by means of an air lift differ from conditions in wells being produced by mechanical appliances, such as bailing, swabbing, and pumping, probably because of different degrees of agitation incident to the several methods.

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Chapter 3

Practical Knowledge of Emulsions

DEMULSIFICATION

Introduction

All small wells and narrow passages through which petroleum passes, together with water and gas from below ground on one side and agitation by pumping on the other, assist in the formation of emulsions. Water-in-oil emulsions, produced together with crude petroleum, occasion a loss in oil to the oil industry. These losses are so great that the problem of emulsion destruction is very important.* Two possibilities of attacking this problem present themselves: (1) devising ways and means whereby emulsification is retarded or decreased, and (2) making dehydration economically possible. It so happens that the quantity of emulsions pumped from oil wells is far in excess of the volume actually dehydrated. Therefore steps should be taken (1) to prevent emulsion formation in wells (proper operation of pumping equipment and application of methods to avoid intimate mixing and agitation of oil and water are advocated); (2) to remove water quickly from the oil on reaching the surface (in the event that an emulsion has formed, dehydration should not be delayed; alteration of the emulsion often induces a more stable state which is rather difficult to treat), and (3) to apply standard economical dehydration methods.

The selection of a proper dehydration method depends greatly upon the qualitative and quantitative characteristics of the emulsion formed, as well as upon the nature of the components emulsified. Three types of crude oil are recognized, and among them there are many grades. The first and most valuable is the paraffin-base found principally in Pennsylvania and adjacent states. The standard A.P.I. gravity of mixed-base crudes from Oklahoma, Wyoming, Colorado and Utah is approximately 30-40; above 40, paraffinic; below 30, naphthenic. Another type of crude oil is the asphalt-base, found principally in California and Texas. Not quite as heavy as the asphaltic base crudes of California is the oil from Texas and Wyoming. Still another type of crude oil is known as the mixed-base,⁷⁶ rich in paraffin wax and asphaltic material found in the oil fields of Baku near the Caspian Sea in Russia. These crudes contain paraffins and are of value as low-cost lubricants.

* The daily production of crude oil in the United States has varied during the last several years within the range of about a million barrels of 42 gallons each. One-quarter of the crude oil produced in the United States is emulsified. About 1/4 of a million barrels of oil are recovered daily.⁷⁶

Many terms, such as "roily oil," "BS," or "bottom settlings," are applied to petroleum emulsions, but they refer in general to a mixture of water, usually a brine, oil, and finely divided silt or other sediment. In these emulsions gravity settling serves to remove the coarsely suspended water from the more concentrated crude-oil emulsion. "Tank bottoms" contain silt, sand, or other sediment, including wax, which separates from the petroleum and sludges to the bottom of storage or other tanks. The amount of water contained in these emulsions varies from traces up to 60 per cent or more, but the majority average about 25 per cent.

Cut oil, roily oil, and "BS" are all water-in-oil emulsions. Sometimes microscopic examination discloses in so-called "dirty water" a multiple emulsion, with water as primary external phase. Similarly, multiple emulsions are found also with oil as the primary external phase. The only essential differences connoted by the various oil-field terms are that "cut oil" and "roily oil" are usually applied to relatively freshly produced emulsions; "BS" is used to designate any emulsion, either fresh or aged; and "bottom settlings" and "tank bottoms" are reserved for emulsions which settle or "sludge" to the bottom of storage or field tanks. The term "BS" is also applied to the emulsion content of any oil as determined in a centrifuge. Included in the terms "BS," "bottom settlings," and "tank bottoms," in their loosest meaning, are quantities of sand, silt, wax, asphalt, or other sediments; but in connection with emulsions, such foreign matter is excluded and the total "cut" of an oil is reported as (1) wax or asphalt, (2) emulsion or "BS," (3) free water, and (4) sand or sediment. A "BS" emulsion usually contains a considerable amount of an emulsifying agent, *e.g.*, asphalt. Whether all emulsions have the same ratio at their "end-point" is doubtful. The recoverable oil in an emulsion often ranges from about 25 to about 75 per cent, as emulsions range from very "loose" to very "tight." The oil content of emulsions corresponding to the amount of oil so intimately associated with the brine droplet as to be recoverable only by resolving the emulsion averages about 50 per cent. Oil recovered from tank bottoms has not always a refining value because of the absence of lighter hydrocarbons and sometimes a high wax content, which makes the pour point of the fuel oil too high; but the latter difficulty is overcome by blending with fresh crude of low pour point. Otherwise the oil recovered from tank bottoms is claimed by many producers and pipeline operators to be of special value because of its superiority as cracking stock.

Bottom settlings are often semi-solid or solid with properties similar to those of semi-solid emulsions or gels, and cannot be broken by any methods or means commonly employed. Because of their water content and lack of fluidity, these emulsions present transportation difficulties to refineries. The Tretolite Company, as well as those major companies maintaining large storage reserves, use successfully a special process for treating bottom settlings. The water content of bottom settlings is not in general much different from that of emulsions from other sources,

except that some of them are likely to contain less free water, owing to the long settling period.

Crude petroleum emulsions commonly occurring in the oil fields contain a continuous oil phase which may be referred to as "free oil," and a water phase of comparatively low dispersion as "free water." In the early days, any emulsion with a water content of less than 10 per cent ⁵¹³ was termed "cut oil," but in current usage no restriction as to water content is recognized. Ordinarily "cut oil" tends to separate into three fairly distinct layers with free oil on top, free water at the bottom, and a layer of bottom settlings. Sometimes there is a fourth layer below the water, consisting of sand or other solid sediment. The completeness of this stratification depends upon the degree of cutting to which the oil is subjected, the gravity and viscosity of the oil, and the emulsifying agents present. Tank bottoms, such as accumulate in storage and occasionally in lease tanks, are sometimes very difficult to treat and are usually more difficult to handle than the original cut oil. Stable "BS" is an emulsion composed of minute water globules dispersed in oil having a diameter less than 0.5 mm.³³¹

The physico-chemical properties of emulsified oils vary. The most common color of an emulsified crude oil is a dark, reddish brown although any color, ranging from yellow or green to gray or almost black, may be found. The color of an emulsion, compared to the color of the oil from which it is derived, is a function of the percentage cut and particle size, the darker colors being due to low percentage cut or large particle size, or both. The color is also affected by the presence of suspended matter, but the effect produced depends upon the particle size and percentage of suspended matter and also upon the color of the material itself. White sand, for example, will lighten the color of an oil or emulsion in which it is suspended.

Another type of emulsion which is difficult to treat is found in the Boryslaw district and is called "Kal ropny"; it occurs also in West Galicia, where it is known as "Czernowica." The crudes derive their names from the rusty appearance of these emulsions. "Kal ropny," as well as "Czernowica" emulsions, contain 40 to 60 per cent brine. Very often these emulsions are considered refinery waste and dumped into rivers. In early days oil producers found it best to dispose of these highly emulsified oils by collecting and burning them in swamps.

All emulsions of oil distillates may be grouped under the heading of "artificial emulsions." Emulsions obtained during the refining process of higher oil fractions are usually very stable. In practice, marketable artificial emulsions are intentionally produced in a refinery from refined fractions of the crude. Petroleum jelly, or Vaseline, is a purified mixture of semi-solid hydrocarbons. Various artificial gels compounded of soft wax and a heavy oil are marketed. Lubricating greases and cheaper greases are examples of water-in-oil emulsions stabilized with soap.

The presence of emulsions in crude oil has its disadvantage since water, which is noncombustible, reduces the calorific value of the oil in direct

ratio to the percentage of water present. Some pipeline companies refuse to accept oil containing more than 2 per cent water, and some mid-continent pipeline companies do not accept oil containing more than 0.5 per cent of water

Demulsification Methods

In choosing the best dehydration method, every well must have its crude oil thoroughly investigated with respect to its characteristics. In general, demulsification may be accomplished by several methods: (1) topping plants; (2) heat treatment (evaporation in open tanks, closed receptacles, etc.); (3) action of chemical agents, nullification of the emulsifying agent by the addition of substances reversing the emulsion type or emulsifying in an opposite direction; (4) desalting; (5) freezing out the continuous phase; (6) breaking down by filtration; (7) electrical dehydration with alternating current; (8) centrifuging. Among these methods three dehydration methods are in general use, *i.e.*, chemical, electrical and heating under pressure.

Heat Treatment

Heating may be regarded as a method employed in resolving an emulsion, as well as an index of the stability of an emulsion, for not every emulsion resolves on heating. But prolonged heating is not advisable. Wischetravski⁶⁴⁴ proposed the so-called "degree of stability" method for petroleum dehydrating practice. According to this method, the stability of emulsions decomposed by heat under one atmosphere pressure for one hour is expressed as a fraction, with pressure as the numerator and time the denominator, 1/1. The emulsion not decomposed is subjected to a second decomposition the results of which are expressed as 2/1.

Dehydration of an emulsified oil by heat is based primarily upon lowering the viscosity and interfacial tension and changing the colloidal properties of the emulsifier. It is difficult to generalize on the specific effect of heat on the properties of the emulsifier, because the effect depends upon the individual case, *i.e.*, the nature of the components involved and the physical conditions of the system. A suitable increase in temperature is combined with a change in the state of aggregation, and the steam and oil vapor formed cause breaks in the surrounding protective films. Heat does not cause the separation of water and oil directly, but rather accelerates it. The accelerated precipitation of water is not solely and always caused by the increase in the difference in the specific gravity of the components due to heating. The specific gravity differential may decrease or be substantially constant, depending on the kind of oil involved. A more rapid precipitation of water on heating may be attributed also to a decrease in the viscosity of the oil. The temperatures to which emulsions must be heated for complete dehydration depend to a certain extent upon the nature of the crude-oil emulsion, and may vary widely. In heating an oil from 15.55-65.5°, the decrease in density amounts to about 3.3 per cent for a mid-continent oil, whereas in heating

water from 15.55-65.5° the decrease in density amounts to 1.9 per cent. For this reason it is possible to obtain a more rapid separation of oil and water at high than at low temperatures. At a given temperature and with oils of the same specific gravity, the one having the lower viscosity will separate more readily from the water. This effect is pronounced when the amount of oil is considerably larger than the amount of water. Increasing the temperature of an emulsified oil from 15.55-65.5° reduces its viscosity at times as much as 55 per cent. The rate of separation varies with the amount of material charged to the still, the size of the still, the amount and degree of dispersion of the water present in the oil, and with the stage of the process. Thus, in determining the optimum treating temperature, gravity differential and viscosity, both as functions of temperature, must be employed.

Heat dehydration may be carried out either as a simple boiling process in an open tank, or in a "topping plant" in which both water and oil are drawn off at the same time. In the first process, the emulsion to be dehydrated is subjected to evaporation in open tanks or pits by superheated steam. This wasteful and costly process of "cooking in vats" went out of use a few years ago. From the standpoint of fuel consumption and oil evaporation, the loss is very great, although many emulsions were dehydrated in this way. The fuel consumption is roughly estimated at 50 bbls. of fuel oil per 1000 bbls. of oil recovered. The loss of oil by evaporation averaged approximately 12.5 per cent on approximately 21° A.P.I. oil. Depending on the nature of the oil treated and the percentage of low-boiling constituents present, the absolute data vary. These facts led to the development of a closed-receptacle plant in which the vapors are condensed and the distillate recovered. The dehydrators used vary in design and construction from systems with topping plants to simple sheet-iron boxes containing coils and having a dome wherein vapors are collected. Some dehydrators are operated with direct heat, others with steam heat. Very often petroleum emulsions were heated by closed pressure steam coils. This practice is bad because the surface of the coil, being hotter than the water in which it is immersed, causes the globules of water coming into contact with it to vaporize, and then almost immediately to condense because of the cooler oil surrounding it. Thus globules smaller than those originally present are formed. The final result of such heating is a separation of a small amount of water-free oil on the surface due to a decrease in viscosity, dispersion causing the formation of a finely divided emulsion, like bottom settlings, which is as difficult to resolve as any untreated crude petroleum emulsion. A more satisfactory method of using heat for promoting coalescence is the submergence of a steam coil in water in the bottom of an emulsion-filled tank. As the water is heated, mild convection currents are set up in the emulsion. By increasing the temperature of the emulsion, the suspended water unites with the water in the bottom of the tank, while the large suspended globules respond readily to whatever treatment they may be given.

High-temperature heating sometimes is a deciding factor in the

resolution of an emulsion. Heating above 100° at ordinary pressure is accompanied by a violent boiling of the water; therefore heating at this temperature is best carried out in an autoclave. Almost all emulsions are decomposed in an autoclave, dehydration being a function of time and temperature. On cooling of the autoclave, part of the condensed liquid accumulates on the walls and at the bottom. If a high-temperature heating is carried out and boiling over of the liquids is prevented, a 100-per cent yield is possible. When a heavy oil is heated to a temperature at which water is driven off, some oil is volatilized and dissipated. The lighter vapors contained in the oil, although sometimes of the highest value, are also driven off by heating. Wiggins³¹⁸ reports that losses due to evaporation in heat treatment of emulsions range from 1.75 per cent at 84° F to 6.7 per cent at 150° F. Corresponding losses in A.P.I. gravity range from 0.65 to 1.99.

Two phenomena, well known to the industrial chemist, accompany heat dehydration: first, a priming or puking of the oil to be dehydrated, a kind of explosion caused by a superheating effect; secondly, foaming of the emulsion. Observations reveal that there is a certain relationship between these phenomena.

Some form of heat treatment is generally used to remove water from oil emulsions; therefore it is of interest to discuss both phenomena, *i.e.*, the priming or puking of the oil and foaming, both of which accompany heat dehydration. If an emulsified oil is heated too rapidly, it usually causes the still to puke. Sometimes puking of the oil is effected by irregularities occurring in heating. Occasionally, when the same amount of the same oil is charged to three stills of the same size, one pukes more readily than the other two.

Marcet³²² was the first to note that the temperature at which water and certain other liquids begin to boil varies with the nature and the state of the surface of the container in which the boiling takes place. These differences have been attributed to a molecular change produced by the surface of the container or by the presence of certain substances. It has been suggested that the part these substances play is to bring about a more or a less perfect contact, or a more or a less close adhesion between the molecules of the liquid and the walls of the container. Whether the conversion of the liquid into vapor is made more difficult or is facilitated is determined by the action of these substances.

Evaporation and ebullition are both molecular phenomena. Both depend upon the action of heat, and differ in the vapor tension produced, as well as in the rapidity with which the change of the liquid into a vapor takes place. In ebullition the change in state is sudden and visible, occurring throughout the system; but in evaporation it is slow and progressive, being restricted to molecules situated at the surface, or very close to it. Any factor increasing the cohesion of the molecules to one another, or their adhesion to the walls of the container in which they are enclosed, will have a tendency to retard evaporation or delay ebullition.

Donny,¹¹⁷ Dufour,¹¹⁹ and Faraday¹⁵² found that water free from air

does not boil until it reaches a temperature of 132° and then explodes. Such water raised to a temperature of 132° under ordinary atmospheric pressure remains as water, but the introduction of the smallest amount of air or steam induces it to vaporize immediately and, at the same time, its temperature falls. Donny assumed that the superheating phenomenon is due to a rupture either in the cohesion of the heated liquid or in its adhesion to the container. Under ordinary conditions, liquids begin to boil approximately at a temperature required by their vapors in order to establish equilibrium with atmospheric pressure. By the effect of ebullition, liquids lose the greater part of the air held in solution, the boiling of the liquid being influenced principally by cohesion and adhesion. The liquid, free from air and heated beyond its boiling point, finally releases vapor explosively, and then a lowering of the temperature restores a momentary quietness to the liquid. Cohesion is the force preventing, or at least delaying considerably, ebullition of liquids free from air. The phenomenon of priming or puking, once started, continues to reproduce the effect with increasing violence. If the principle that the liquid must be free from air in order to produce this phenomenon holds true, then the latter may be avoided by passing a gas through the liquid. Donny's experiments reveal that this is true only in certain cases. De la Rive⁴³¹ and Dufour¹¹⁹ studied the change in state under the influence of temperature. They pointed out that the presence of a foreign substance in a liquid may hasten evaporation, assuming that the change in state does not necessarily occur when a vapor tension equal to the outside pressure is produced by heating the liquid, but that it may occur partially because of certain changes in the molecular state when the liquid is brought into contact with them.

The solid contacts tend to promote vaporization at a minimum temperature. Because of this, noticeable differences in boiling point are observed when water, alcohol, or sulfuric acid are heated in a glass or in a porcelain container (experiments by Donny,¹¹⁷ Marcet,³²² and Magnus³¹⁵), or when heated out of contact with solid particles. In some cases it appears that the contact of solid particles is a determining cause of the change in the state of fluids. If a globule of liquid comes into contact with a solid particle entrained by currents induced by heat, or with the walls of the container, sudden formation of a bubble takes place. If water is mixed with sand,⁴³¹ with a liquid layer a few millimeters thick, the water evaporates more rapidly than the same quantity of pure water. Thus the temperature of a water-sand mixture evaporating in air is lower than that of water exposed alone under the same conditions. Water containing sea salt also evaporates less rapidly, producing a smaller degree of cooling by its evaporation than pure water under the same conditions.

Kenrick²⁰⁶ and his co-workers studied the superheating phenomenon of liquids. A study was made of the extent to which liquids may be superheated and the physical conditions under which superheating is possible, *i.e.*, where temperatures are equal to or higher than those where the elastic force of the liquid produces equilibrium with the external pressure.

The question regarding the location of the ebullient and superheating influences also appeared of interest to these investigators. They assumed that ebullition takes place locally, either at a few fixed points on the walls of the container, or from particles suspended in the liquid from which streams of bubbles actually rise. If this is true, the superheating effect should depend on the ability of the liquid to wet the material which serves as a nucleus.

Kenrick found a gradation in the effectiveness of the nuclei present. Some of them caused ebullition when the liquid was slightly superheated; others were effective only when it was heated to a higher temperature. Experimentally, it was not clear whether there was a real temperature limit or merely a rapid shortening of the time interval with increase in temperature. He also found that the smaller the container in which the liquid is heated, the higher the temperature to which it could be heated without boiling. Wismer⁶⁴⁷ calculated the diameter of a spherical particle acting as a nucleus enclosed by bubbles and found that it was equal to 5×10^{-7} cm. Calculation of the pressure in the bubbles gave a value of about 12.5 atm, corresponding to a temperature of about 130° (extrapolated). Gilbert¹⁸⁰ calculated the amount of vapor in a bubble whose pressure, caused by surface tension, balances the outside vapor pressure. Quantities about one hundred times greater than those corresponding to the ordinarily accepted molecular dimensions were determined. This led Gilbert to the conclusion that liquids which can be heated to temperatures corresponding to abnormally high vapor pressures are those which are abnormal in possessing high association coefficients, as in Table 1.

Table 1

Liquid	Highest Temperature (°C)	Pressure (mm)	Boiling Point (°C)	Association Coefficient
Ethyl ether	143	11,500	35	1.0
Ethyl alcohol	201	22,700	78	2.7
Methyl alcohol	180	20,100	63	3.4
Chloroform	173	11,000	61	1.0
Acetone	174	14,400	56	1.3
Carbon disulfide	168	11,700	46	1.0
Water	270	41,200	100	2.3-3.8
Sulfur dioxide	50	6,300	-10	1.0
Benzene	203	11,200	79	1.0
Chlorobenzene	250	8,300	132	
Bromobenzene	261	6,100	156	
Aniline	262		183	
<i>m</i> -Xylene	235		137	

Wismer⁶⁴⁶ determined the pressure-volume relations for ether at 121°, 128°, and 134°, and corresponding pressures above 30 atmospheres to as low as 1 atmosphere. He made similar measurements with ethyl chloride at 99°, 110°, and 117°. The P-V curve in both cases appears to be almost a straight line, and there is no sign of more rapid curving as the limit of superheating is reached, although in both cases the temperatures reached

at atmospheric pressure were above the maximum calculated from Van der Waals' equation.

The most characteristic points in the superheating effect are the extent to which superheating of a given liquid is carried out and the time at which a liquid is kept under these conditions. It has been observed that these characteristics vary from one experiment to another. Kenrick, Gilbert, and Wismer²⁰⁷ attempted to work out these questions concerning superheating phenomena. Previous work¹⁹ indicated that the superheating of liquids is closely allied to the "stretching" phenomena of liquids,³⁴² as well as to supersaturation of gases.⁶⁴⁷

Supersaturation is favored by long heating of a solution at high temperature. Liquids saturated with gases at concentrations corresponding to a pressure of over 100 atmospheres showed that when the pressure was reduced to one atmosphere no bubbles were formed in the liquid. In the case of superheating of liquids, Kenrick, Wismer and Wyatt observed that with a rise in temperature there is a very rapid shortening of the time interval between the lowering of the pressure and the formation of bubbles, in spite of the fact that the absorption coefficient of the gas decreased but little with temperature rise. There is definite evidence in favor of the old theories of the superheating phenomenon, namely, that liquids must be free from gases and air to exhibit superheating effects.

Krebs²⁷⁸ removed air from water by mixing the latter with alcohol (about three times the volume of water) and boiling down the mixture to a small volume (the boiling point increased steadily to 107°). When a very large flask was used and the mixture evaporated to a small volume, the boiling point could be still further increased. In boiling this water-alcohol mixture, Krebs observed for the first time the coexistence of superheating and foaming.

There is a certain analogy between the liquids and emulsion systems in respect of the superheating phenomenon. In emulsions the superheating effect finds its explanation in the behavior of the interfacial phase. As early as 1836, Magnus³¹⁶ showed that water with oil poured over it shows a considerably delayed ebullition. If oil is poured upon water, the explosive boiling is much more violent. Rideal⁴²⁹ proved that evaporation of water from a surface is considerably diminished in the presence of fatty acids, such as stearic and oleic, as compared with evaporation from a free surface.²²² An increase in the concentration or in the pressure upon the surface may also delay evaporation. It is to be expected that surface layers in a condensed or a vapor state primarily influence evaporation. When an oil-in-water emulsion is heated, the continuous phase covered with a thin layer of oil must be heated to a higher temperature than the boiling point of water in order to initiate boiling. A sudden decrease from a higher to a lower boiling temperature may be attributed to a change in the Brownian movement during the heating, causing a cessation in the continuity of the interfacial oil skin and a decrease in temperature.

Taylor,⁵⁰⁷ in his article on "The Structure and Decomposition of

Liquid Skins," states that monomolecular layers actually do have thick spots which interfere with their stability. It is possible that the problem as to whether skins in the interface are factors in the explanation of the superheating phenomenon in emulsion systems may be solved experimentally, using dyestuffs. Frumkin, in his work on the spreading of dye substances on a water surface, proved that the presence of two competing substances on the same water surface can be demonstrated. When a drop of oleic acid is placed on a water-crystal violet dye surface, the oleic acid molecules displace the dye molecules and the dyed layer sinks streaming to the bottom. On a water surface previously covered with an oleic acid film, the crystal violet dye particles remain colorless upon the surface. Tetraiodofluorescein behaves similarly. Perhaps by means of such a dye it will be possible to prove whether superheated water in a water-oil emulsion is actually covered with a thin layer of oil, causing a decrease in evaporation, depressing ebullition and, consequently, producing the superheating effect during dehydration of crude-oil emulsions.

Foaming is a phenomenon closely connected with heat dehydration of emulsified oils. Very often emulsions in their original state cannot be subjected to distillation without foaming. Foaming is, of course, undesirable, not only because redistillation is necessary, but also because of the imminent fire hazard. It is believed that incipient foam formation with rapid breaking down of the foam itself plays a significant role in the dehydration mechanism. Pressure and high temperature are two factors which favor dehydration, and at the same time reduce the foaming tendency of the emulsion system. Pressure weakens the foam film structure; at higher temperatures the ability of the oil to make and to maintain individual foam lamellae is decreased. In petroleum emulsions the emulsifying agent is usually asphalt, "soaps," or mineral matter, and the decreased foaming with increase in temperature is due less to a change in composition at the temperature at which foaming ceases than to a decreased protective action.

A number of experiments have been carried out by Egloff and Berkman¹⁴⁰ on foam formation in heat dehydration of emulsified crude oils. The first question arising in connection with the problem concerns itself with the conditions under which foam originates.

(1) It was found that for the same temperature more water is separated out from an emulsion when a vapor space is present than when no vapor space exists. When one-fourth, one-half, or three-fourths of a still's capacity was charged with a crude-oil emulsion containing 36 per cent of water and heated to 121.1° under 2.74 kg/sq cm pressure, 10-12 per cent of water separated out. When a full charge was maintained at the same temperature, but with a pressure of 3.31 kg/sq cm, only 6 per cent of water separated out. The lack of vapor space prevents substantial foam formation which probably accounts for the difference in the dehydration effect.

(2) A series of tests was made with 16 samples of emulsified California oils to determine their foaming properties. The oils were charged

in beakers, immersed in a glycerin heating bath and the foaming properties and height of the foam noted. The oils treated had a water content ranging from 6 to 69 per cent. The temperature of the glycerin bath in these comparative tests was maintained constant at 177°. It was found that under the temperature conditions existing the foam column in the emulsified crude oil varied from one and one-half inches to over five inches in height. It is interesting to note that a mixture of California oils No. 6 and No. 2, taken in equal portions, showed a foam column height greater than when the oils were subjected singly to the same heating. California oil No. 6 with 6 per cent water: foam height, 3.8 cm.

California oil No. 2 with 30 per cent water: foam height, 10.5 cm.

A mixture of the two oils in equal proportions: foam height, 11.8 cm.

This indicates, as far as these tests are concerned, that the foaming properties of emulsified crude oils are not additive when mixed. One would expect a decrease in the foam column of California oil No. 2 due to the addition of an oil having a low water content. However, this is not the case. As a matter of fact, the diluent oil No. 6 did not decrease the foam column, but actually increased it.

(3) Distillation of crude oils of varying origin revealed that foam formation in emulsified oils depends greatly upon the nature of the crude oil. The oils compared were from Casmalia, Santa Maria, Lompoc and Efsen oil wells. Casmalia oil is very persistent in foaming; Santa Maria oil foams slightly; Lompoc oil foams strongly, and the foaming of Efsen oil shows explosive characteristics.

Some emulsified oils distill quickly and then begin to foam after distillation has proceeded for some time, whereas other oils foam violently from the beginning of heat application.

Lompoc emulsified oil from Efsen well No. 10 produced more foam at 149° than any Santa Maria crude oil tested, but Casmalia crude oil was the most persistent foam producer of all those tried. It was found further that the Lompoc oil acted in an explosive manner when heated. To overcome the violent bumping of this oil, gasoline was added to it and the foaming test conducted. The oil evaporated in a much less violent manner, but spattered and sputtered during the heating, and the foam was not persistent. This indicates that the gasoline added to the Lompoc emulsified oil has a marked influence upon its foaming and evaporating properties.

Some emulsified oils, upon application of heat, form relatively small foam bubbles, and others produce large bubbles.

(4) The effect of temperature on the foaming properties of an emulsified oil was studied as a function of the depth of the liquid placed in the tube. The oil investigated was Santa Maria crude oil containing 29 per cent of water. The procedure was to charge glass test-tubes 2.24 cm in diameter and 20.3 cm long with 1, 2, and 3 cc of Santa Maria emulsified oil, and to immerse them to 17.8 cm of their length in a heated glycerin bath. After the glycerin bath had reached the desired temperature, the tube containing the emulsified oil was introduced. At the

beginning of the test, the emulsified oil distilled quietly with little foaming. As vapors passed from the top of the tube, a time was reached when the foam, which started in a fine division, became coarse and persistent. The foam rising in the tube became at times somewhat irregular, seeming to give a breathing action, but finally attained a maximum and then gradually subsided. The maximum height which the foam column reached was recorded, and all comparisons were made in a similar manner.

It was found that the foam column of the Santa Maria emulsified oil increased as a function of the depth of the oil in the tube; it also increased, as a function of the temperature employed, to a maximum which was attained at 140° glycerin bath temperature, the foam column decreasing as the temperature of the bath reached 176°.

Table 2 gives the order of foam formation as a function of temperature variation, and depth of liquid employed during this series of experiments:

Temperature of Bath (°C)	Volume emulsified oil used		
	1 cc	2 cc	3 cc
125	16	19	32
140	32	52	80
150	34	49	70
160	26	42	50
176	23	33	44

(5) Finally, from a series of tests in which California emulsified crude oils were dehydrated, it was ascertained (a fact already indicated by Krebs²⁷⁸) that foaming in heat dehydration was combined with the superheating effect discussed previously, as well as with self-cooling. Usually, during the heating of California emulsified oils, the temperature rose quite rapidly to a little above the boiling point of water, where it remained relatively constant for a time until a portion of the water was distilled from the oil, the temperature rising until a maximum was reached when the oil was dehydrated with a few fine drops of water still dispersed in the tar residue. With several of the emulsified crude oils, a marked departure from the behavior just described was noted.

Santa Maria crude oil from Rice Ranch well No. 2 showed a distinct superheating effect with rise in temperature, followed by more or less foaming, a drop in the temperature of the oil taking place despite the fact that the oil was still being heated. In other words, water was apparently held in the oil above its boiling point and, by this superheating, suddenly formed steam with cooling taking place in the liquid. There would therefore be one of the following mechanisms: either the emulsion system during this period absorbs heat from the oil faster than it can be supplied from an external source to the extent of producing a cooling effect (manifested by an actual drop in the temperature of the oil); or under critical temperature conditions the protective films are ruptured; or else chemical changes occur in the emulsifying agent (a dissociation of the hydrates of the hydrocarbons present in the emulsified crude-oil system), which remove heat from the system, thereby cooling it.

Roberts* suggests considering the effect as entirely analogous to those observed in running cooling curves on crystallizable systems, in which the heat of fusion is suddenly liberated, thereby arresting the normal rate of cooling or even causing an increase in temperature. In the case of emulsions the temperature decrease is due to sudden abstraction of the heat of vaporization, with consequent cooling, while the superheating is caused by the increased boiling point of water under the high internal pressure existing in small emulsion droplets.

In Table 3 are indicated on two samples the three phases in heating characteristics of a Rice Ranch, Santa Maria, crude-oil emulsion which exhibits foaming. The data give complete support to the latter explanation.

Table 3. Foam in Heat Dehydration Combined with Superheating Effect and Self-cooling

Phases in Heating Process	Temperature (°C)	Characteristics of Foaming
<i>Oil Sample No. 1:</i>		
I Phase	Up to 111.1	Little foaming
II Phase	Drop in temperature to 102.2 constant for a time	Foam column rising.
III Phase	Rise in temperature from 102.7 to 104.4	Foam column starting to collapse
<i>Oil Sample No. 2:</i>		
I Phase	Up to 107.2	Slight foaming
II Phase	From 107.2 to 102.2	Foaming increasing
III Phase	From 101.6 to 111.1	Foaming rapidly receding
	At 150.0	Foaming almost zero

Comparatively few patented types of heat dehydration equipment take into account the foaming ability of oils, even though practice shows quite a number of cases in which foaming has occurred during dehydration. Seyffert⁴⁶¹ suggests using a spiral heating apparatus connected with an evaporator to prevent foaming of liquids during vacuum distillation. Paulik³⁷⁶ removes foam from continuous "Malaxers" by utilizing angular troughs leading into a central container. Spilker⁴⁹¹ conducts distillation by leading the liquid over a series of vertical plates against a current of vapor to prevent foaming. Nauman³⁶⁰ recommends a foam-prevention device. Prutzman⁴¹⁸ describes a dehydrating apparatus for foaming oils comprising a retort, a steam coil near the bottom of the retort, and a second coil, through which oil is introduced into the retort, located above the steam coil. Pressure in the retort is atmospheric. Treating the emulsified oil consists in driving off the lighter fractions of oil, as well as water, and forcing small jets of the emulsified oil against a heated body beneath the surface of the oil. In treating oils which foam, foaming occurs in the dehydrating tube, from which the vapors emerge through the restricted discharge openings in amounts insufficient to disturb seriously

* Roberts. Private communication.

the oil mass in the retort. Jetting of the heated oil aids the dehydration of foaming oils.

Foam may be broken by passing it through two series of grating plates, one series of which is adjustable with reference to the second series, as patented by Kichalik.²⁶⁸ Foaming during steam distillation, or during the determination of water by the Bidwell-Sterling method of xylene distillation, is prevented in many cases, according to Hart,²¹⁶ by the addition of a mixture composed of 3-5 g of sodium acid sulfate, 2-5 g of lump rosin, 5 cc of oleic acid, a small piece of paraffin, some mineral oil, a solution of a barium or a calcium salt, and a few drops of amyl alcohol.

Dehydration by heating of crude oil or water containing high-boiling tars or highly viscous liquids of a high critical point is accompanied by evaporation of water from the heated liquid by the formation of foam. Bringing the foam into contact with a liquid which has a high critical point and a temperature higher than that of the foam which it dissolves when caused to flow²⁷⁶ has been suggested.

W. Ostwald and A. Siehr³⁶⁹ proposed a new method and apparatus for circular destruction of foam, whereby the foam originating in the system is taken up and dehydrated. The method is claimed to be suitable for resolving the difficult and not readily destroyed foams, *e.g.*, albumin and stearate foams. By resolving the foam a stearate sol is formed.

According to Belani,⁴³ the use of protein, gelatin, dextrin, and casein preparations in the manufacture of paper often causes foaming. Petroleum, fat, milk, peanut oil, whale oil, oil of cloves, various vegetable oils, and alcohols of the fatty acid series have been found to decrease foaming. A mixture of linseed oil and alkali is very effective in preventing foaming. Alkali glues have been found to foam more strongly than neutral bone glues. When heated too strongly, animal glues give off protein decomposition products which cause profuse foaming.

Russell⁴⁴⁵ observed that foaming results when sludge does not go beyond the first stage in digestion, or beyond the period of intensive acid production during the decomposition of soluble carbon compounds and the breaking down of cellulose. To prevent foaming, the baffles and the slot below them should be kept clean so that putrefaction does not occur in the sedimentation compartment. Floating material should be removed, and scum in gas vents broken up and pushed down into the digestion chamber. Removal of some of the sludge may reduce or stop foaming. Addition of lime to maintain the pH above neutral is recommended. A small dose of chlorine added to the sewage entering the tank reduces the tendency to foam.

Meyer,³⁴⁴ reviewing available methods for reducing undesirable foaming in technical operations involving colloidal solutions, states that the addition of a number of organic liquids to a foam formed in a glue solution, for example, showed that fatty acids were more effective in destroying this foam than their corresponding alcohols. No relation whatsoever has been found between the surface tension of the liquid and its power to destroy foam, but in homologous series the prevention of foaming

increased with an increase in the molecular weight of the compound. With an increase in the concentration of the glue, the foaming ability reached its maximum.

Several methods have been proposed for the prevention of foam formation or its destruction after it has been formed. Boutarie⁵⁷ discusses the destruction of foam in connection with emulsion practice. For the prevention of foam, the Electro-Chemical Engineering Co.¹⁴³ uses two electrodes placed in a liquid metal touching the foam bubbles. When the electrode is connected with a current, the foam bubbles are electrically discharged and the foam is destroyed. This is explained by the ability of colloidal solutions to adsorb ions.

The most common foam-breaking or foam-preventing method is that of adding a chemical agent which acts in the desired direction. Investigating the foam-preventive action of various oils, Worobjew⁵³ found that that of castor oil is greater than that of linseed oil; this action is also greatly increased on oxidation. The velocity of foam destruction proceeds parallel with the decrease in surface tension of the solution. Clarkson⁸⁵ prevents foaming by adding to the foam-forming liquid less than 1 per cent of liquid organic compounds, fraction 133-210° or 160-210°, obtained by high-pressure hydrogenation of carbon monoxide. These organic compounds may be mixed with benzene. According to another patent,⁸⁴ the decrease of foam formation is brought about by adding alcohols, obtained as by-products in the catalytic pressure synthesis of methanol, when all ingredients boiling below 200-225° are removed. The action of the dispersion medium may be increased by adding a fraction boiling between 130-200°. Ethyl alcohol, methyl alcohol, acetone, pine oil and castor oil, etc., are also called dispersion agents.

Schmidt^{270a} considers liquid and paste-like sulfonation products as foam-preventing agents. National Oil Products Co.³⁵⁹ adds to the foam to be destroyed paraffin, fatty acids, pine oil dissolved in water with a suitable dispersion agent, such as sulfonated oil or tallow; for example, 40 parts of paraffin and 10 parts of aluminum stearate are heated until dissolved and then 50 parts of sulfonated tallow is added. The mixture is heated to about 75° for 15 minutes with constant stirring, and then cooled.

Bendieu⁴⁵ recommended prevention of foaming in microkjeldahl determinations by the addition of traces of cholesterin (3-5 drops, 0.5-per cent alcoholic solution per 20 cc). Larger additions would cause formation of foam again.

Standard Oil Development Co.⁴⁹⁶ prevents foams in mineral oil-water emulsions resulting from oil-soluble sulfonates as well as from ammonia or ethanolamino salts. To the emulsion system are added 0.2-2 per cent of saturated high molecular fatty acids, such as stearic acid or acids originating in oxidation of paraffin. The amount added is related to the amount of the emulsifier.

It has been found that frothing of mud (degasification) can be minimized or completely eliminated, and petroleum emulsions simultaneously

resolved, by the introduction of isoamyl alcohol. The amounts of the latter needed are given in a diagram.²⁸⁰

Methods and Equipment for Heat Dehydration of Hydrocarbon Emulsions. The heaters for crude-oil emulsions are classified as follows: (1) high-pressure steam, (2) low-pressure steam, (3) coil-type boiler heaters, (4) direct-flame boiler heaters, and (5) pipe heaters.⁸⁵²

Concerning the advantages and disadvantages of these types it is said ^{328c} that high-pressure steam heaters are cheap to install and maintain, and occupy only a small space. The cost of the steam is high. Low-pressure steam heaters are generally made from old boilers and a heat exchanger, and are suitable for locations where boiler feed-water is expensive or corrosive. The installation is cheap, but the heater used must contain more heating surface, owing to the lower heat-transfer rate. Steam and condensate return lines must be larger than when high-pressure heaters are used.

Steam heating of the emulsion in a tank is not considered good practice, because of the possibility of the tank boiling over and of the loss of light fractions, except where the crude oil is heated to drop out sand or to reduce its viscosity for pumping. Coil-type heaters are essentially the same as low-pressure steam heaters in which the heating coil is placed inside the boiler. It may be made from oil boilers by removing the upper half of the tubes and installing a new tube-sheet welded in to take the oil tubes. A baffled head is provided to cause the oil to make as many passes as possible through the heater. The advantages and disadvantages of this system are similar to those of low-pressure steam heaters. The coil-type heater should be more efficient than the low-pressure steam heater as there is less surface for radiation, the heating coil being immersed in the fluid inside the boiler. The direct-flame boiler heaters are boilers which have been converted to oil heaters. They are either the small vertical, locomotive fire-box, or return tubular types. The boiler heater holds a relatively large volume of fluid as compared to other types of heaters, and therefore is frequently used for heating oil on the flow line of wells. When properly installed they give very little trouble.

Pipe heaters are of two types, the large heater that follows the design of pipe stills for refining work, and the small unit made from casing and pipe available on the lease. The pipe heater is particularly applicable to heating large quantities of oil where the flow is continuous. Its efficiency is higher than that of the boiler-type heaters, and is comparable with that of the coil type. The pipe heater requires less space than any other type except those using high-pressure steam. Oils of any gravity and containing sediment can be heated in these heaters provided the flow is high enough to prevent deposition of sediment in the tubes. The small pipe heaters are relatively low in cost and may be used for continuous flow.

Every heat dehydration plant must be adapted to the type of crude oil to be heat-treated. Wagner,⁶¹⁶ treating Mexican crude of 9° gravity with 20 per cent bottom settlings, states that this oil is a typical example

in which gravity and viscosity make the use of any chemical treatment difficult, since this depends on an intimate admixture of the reagent with the disperse phase.

Closed steam coils are not adapted to the high temperatures necessary for the heat resolution of an emulsion. Neither are open steam coils suitable, for the steam ejected directly into the oil produces emulsification to a greater degree. Wagner found a tube still apparatus more satisfactory. Open heater pits equipped with closed steam coils were constructed adjacent to a large earthen reservoir holding the stock emulsion. This stock emulsion was drawn into the pits and heated to 160° F to separate the greater part of the free water carried with the oil. The oil from the heater pits was pumped through a preheater constructed of 16-inch pipe containing superheated steam coils and heated to 240° F; a part of the water separated in the preheater. From the preheater the oil entered the tube still in which the oil and the emulsion were subjected to a temperature ranging from 280° to 340° F, depending upon the pressure maintained in the still. The still was washed with fresh water every 24 hours to remove the salt deposits. When the alkalies contained as impurities in the oil pumped from the wells came into contact with the oil at or above 260° F, stable, soapy substances were formed. The operation in this type of dehydrator⁶³⁴ is dependent on temperature, that is, when the temperature of the oil and impurities is raised to 260° F, they are then drawn off into a separator and allowed to cool. After the oil and impurities have separated they are readily removed from the tank.

Steam is usually employed as a heating medium and generated in a plant separate from the dehydrator. In the Arnold¹² dehydrator, the steam-generating plant and the dehydrator are arranged as a unit structure, the pipes conducting the oil being located inside the steam-chamber of the boiler. In treating oil mixed with water and gas, Daughdrill¹⁰² used an apparatus consisting of a tank with oil and water outlets at different levels and a separating drum having a gas outlet. Means for delivering the emulsion into the drum to separate the gas from the mixture are provided. This tank is further provided with a pipe for conveying the mixture from the drum into the lower compartment of the tank, with delivery pipes extending from the first pipe having an outlet into the tank, with steam nozzles inside of every delivery pipe, with a steam pipe connected with every nozzle, and with a water inlet pipe into every steam pipe.

Wilke⁶³⁸ proposes the following method for the dehydration of petroleum hydrocarbons. The emulsion is heated in a container to 100°. Water and light hydrocarbons are converted into vapor, while heavier hydrocarbons settle out from the liquid. The vapors given off are condensed by cooling, and the condensate, consisting of light hydrocarbons and water, is recirculated into the evaporator to the coolest section of the bottom. Since renewed evaporation due to the low temperature does not take place here, the water settles at the bottom, whence it is drawn off. The light hydrocarbons rise and mix with the contents of the container.

As a result of this back flow of the light liquid condensate into the liquid which is to be dehydrated, it becomes more fluid, facilitating separation of the water.

Tatman⁵⁰⁶ patented an improvement for oil separators, applicable to a device for treating crude oil direct from oil wells, for separating water from the oil. The apparatus comprises a coil for circulating oil, a heating coil enclosing the circulating coil, and a water tank arranged above the heating coil. The ends of the heating coil are connected with the top and bottom sections of the tank, and a by-pass establishing communication between the portions of oil at both ends is arranged in the coil at a point below the tank. Wikner⁶³⁵ provides a heating container for coal-tar and crude petroleum with means for keeping the liquid contained in it at a constant level. A heating coil through which the hot liquid circulates is located just below. The many pipes leading from the interior of this tank have openings just above the level of the liquid surface in the tank. The water vapor or other vapors pass down through the bulk of the liquid, the latter being heated, and the vapor is condensed.

Gardner^{189a} describes a crude-oil treating tank of any desired capacity in which the mass is passed through a coil and the impurities separated by heating. Baum's⁴⁰ dehydration equipment is constructed principally of an outside casing with a conical double-walled shell arranged on the inside, the diameter of which increases downward to provide a heating chamber open at its lower end containing a heating coil and a feed pipe leading into it. A continuous flange formed on the upper side of the conical shell serves as a receiving receptacle. The oil is heated to the temperature necessary to separate it from the water.

Conway's⁹⁴ device for heat treatment of crude oil separates from water not only oil, but impurities as well. The oil separator has a chamber for water provided with plates at both top and bottom. A fire-box is arranged below the bottom plate and a smoke-box is located above the top plate, both being connected with a chimney. Straight heating tubes for the water extend between the two plates. Perforated spray pipes are placed vertically between the lower parts of the heating tubes in the water space. The inlet pipe for oil projects through the side of the container. The water is heated to a predetermined temperature.

Brady⁵⁹ describes a dehydrator consisting of a tank, a valve at one end of the tank and a second valve at the other end of the tank. The first valve regulates the liquid level in the tank; the second opens at a higher level of the liquid in the tank. Means are provided to adjust these valves so that they can give variations of their maximum open positions. Pollak's⁴¹² apparatus and process dehydrates oil as rapidly as possible and at the lowest temperature permissible to avoid distillation of the oil. The dehydration action varies according to the quantity of the emulsion and the flow of the oil to be treated. A chamber with a perforated plate at the top and a series of horizontal perforated plates at the bottom from which oil drips comprises this apparatus. Steam coils are arranged in staggered positions over which flows the oil to be dehy-

drated, the steam supply for these coils being controlled. Condensers and individual chambers for receiving the liquids condensed are provided. Vaporization under atmospheric pressure takes place in this dehydration process.

Hurst ²⁵⁰ patented a type of heat dehydrator causing a rapid coalescence of the minute droplets of water contained in the treated emulsion. The emulsion passes from the coil located in the treating chamber and is conducted through pipes at a temperature of 150 to 180° F. The oil is heated effectively with a minimum heat loss due to the use of a particular type of fire-box and coil construction, as well as to the arrangement of a preheater above the treating chamber so that no heat remains in the combustion products. The tubes in which heating takes place are provided with sinuous baffles; the water in them is evaporated, preferably by heating to temperatures ranging from 200 to 230° F. The "Metan" dehydrator for breaking crude-oil emulsions, described by Burck, ⁷⁷ is a combination of a preheater and separator. The crude-oil emulsion is drawn by suction into the preheater, which contains steam coils. From the preheater the hot emulsion is pumped into the separator which contains baffles and is kept at a pressure of 10 atmospheres. The oil separates at the top and is forced through a coil in the bottom of the preheater to a storage container.

Oil recovery from aqueous emulsions recommended by Erfurt's ^{108a} method consists in allowing the aqueous emulsion to flow slowly over a suitable heated surface provided with cross bars where the disintegrated emulsions are recovered in a receptacle and in which the oil is separated from the water.

Novotney and Hunter ³⁶⁴ claim that petroleum emulsions are resolved by causing them to flow in a looped stream, the branches of the loops being in heat-exchange relation. The stream is heated in the turn of the loop, so that the emulsion rises through an accumulation of heated heavier components previously separated at a lower temperature.

According to Bailey, ²⁹ crude-oil emulsions are first heated in a heat exchanger and by means of water vapor indirectly heated to about 100°, after which they are passed through a bundle of tubes cooled from the outside. The emulsion is broken and the water withdrawn from below the bend containing the bundle of tubes.

Volokh ⁶¹⁴ discusses the difficulties experienced in various refineries through the contamination of crude oil with water and other admixed substances. The ash content of crude oils is stated to be lower than the total of admixtures composed mainly of naphthenic acids or their soaps. These admixtures are separated by heating the crude oil in heat exchangers.

Hering ²⁸⁵ reports a process for dehydrating hydrocarbons by circulating oil through a coiled pipe heated by steam. The temperature is maintained constant and the degree of dehydration is estimated from the amount of the condensate in the condenser. Hot water is used as the heating medium and low-pressure steam is provided for the operation of a pump, which produces a regulated vacuum. Asiatic Petroleum Co.,

Ltd.¹³ proposed a method and equipment for dehydrating hydrocarbon emulsions in which salt-containing crude petroleum emulsions are led continuously into the top of a vessel partially filled with hot dehydrated oil (about 100°). Water is evaporated and the precipitated salt floats in the oil instead of forming a solid crust on the walls of the vessel. The dehydrated oil is conducted continuously by pumps through a heater.

Kauffmann²⁰³ patented the interior construction of a cylinder provided with openings at the bottom. The liquid in the cylinder is maintained at a lower temperature than that on the outside, which serves to prevent priming. Steam passed through an upper coil in the apparatus heats the emulsion to the desired temperature. A special arrangement on the steam coil functions as a safety valve to prevent the accumulation of condensed steam in the steam coil.

Dyer,¹²³ in his work on dehydrating hydrocarbon oils, used a series of closed containers, each of which was provided with a tubular heat-circulating system equipped with vertical and longitudinal baffles arranged to form a torturous path for the oil. Heat from an outside source was supplied to the tubes of one container, vapors from this receptacle passing through the tubes of the adjoining container; this process continued for the entire series. According to Carrol,⁸¹ a warm or hot emulsion of fat and water is placed in a chamber provided with an internal, contracted neck fitted with a short tube in which the fat solidifies, the space surrounding the top of the neck being filled with cold water. After the fat has solidified, it may be removed by drawing a scraping disc through the tube. The container into which the emulsion passes at the bottom may be provided with a horizontal partition having an opening over which funnels are inverted to collect the solidified substance. The top of every funnel is flared outward and all funnels are united by shallow channels.

Hopkins²⁴⁶ dehydrates refuse oil to a point where it is "cut" to less than 3 per cent (Gauger's test), removing at the same time the greater portion of foreign matter which it may contain. This crude oil dehydrator includes a casing divided into upper and lower oil chambers with a heating chamber between. Many open, bent tubes connect the oil chambers, every tube itself having many tubes mounted concentrically in it and spaced apart to form many heat and oil passages. The heat passages are connected, forming a continuous conduit having both heat inlet and heat outlet openings. Although live steam is utilized as a heating agent, any other heating agent, such as heated water or air, may be employed with good results. There are condensers connected to the casing to handle the vapors arising from the heated oil.

Twine,⁶¹⁰ discussing the dehydration of water-gas emulsions in Nicholls plants in which about 1,750,000 gallons have accumulated over a period of years, points out the failure of such methods as direct heating, steam-coil heating, and others, emphasizing the fact that in order to dehydrate these emulsions successfully it is necessary to maintain (1) constant water content of the emulsion to be treated; (2) constant temperature of the feed to the still; (3) regularity of the feed to the still;

(4) uniformity in heating the still; and (5) the output of tar below 0.5 per cent of water.

Williams⁶⁴⁰ developed a unique method for the removal of water from crude oil. The process involves a closed system both for the emulsion to be treated and for the steam employed for heating. The apparatus consists of a series of units of three pipes telescoped together. The cold emulsion enters the middle pipe of the first unit, passing through every unit until the last pipe is reached where the final temperature is obtained. Steam is applied to the inside and outside pipes of the last two units. From the middle pipe of the last unit the emulsion, after reaching the temperature required to break it, reverses its course and passes back through the unheated inside and outside pipes. Heat is applied to the incoming cold emulsion, leaving the system at a temperature slightly above that of the original cold emulsion.

A plant for dehydration of highly contaminated petroleum has been described by V. P. Bat.³⁵

An emulsion-treating plant capable of handling 20,000 barrels of fluid per day has been constructed by the Magnolia Petroleum Company. The plant consists of two 104 h.p. boilers, a number of tanks, six 185-barrel treating units, pump station, and auxiliary equipment. The fluid passes through a series of coils at the boiler in which it is heated to about 180° under a pressure of 300 lbs. From this point the fluid passes to the treaters without cooling and the basic sediment and water are run to pits and the oil to a gun-barrel separator.⁴¹⁴

Th. H. Jackson²⁵⁴ describes an apparatus for dehydrating tar emulsions in which the emulsion to be dehydrated is heated by live steam. J. W. Hays²²¹ patented a heating apparatus for breaking down emulsions. Any kind of emulsion can be handled and, if necessary, the temperature of the liquid may be raised high enough to vaporize some of the heavier oil fractions as well as the lighter ones. The apparatus consists of a combined heater and dephlegmator. The heater comprises an elongated furnace chamber, placed in a vertical position, and means for producing heat in a radiant form in the upper part of the chamber by flameless catalytic combustion of a fuel. In the lower part of the chamber is a discharge opening for combustion products. This chamber is surrounded by one through which the emulsion to be treated is circulated in an upward direction. Between the upper part of this chamber and the dephlegmator is a pipe connection.

A modern steam plant for breaking and settling "BS" emulsions comprises a battery of at least three tanks. In the first tank or "gun barrel" the crude emulsified oil is heated with steam. Care is taken to heat the oil to the proper temperature, which is thermostatically controlled. The temperature for breaking emulsions was found to vary from 122° to 160° F, depending on the type of crude and the nature of the emulsion. From the "gun barrel" tank the oil flows to a second tank where its heating is continued; it then flows to a third tank in which traces of emulsion not yet removed are broken up. From the third tank the oil flows

into storage tanks where it settles to remove the last traces of "BS" and water. This process is continuous and can be carried out without interruption for weeks and months. The salt water accumulating in the "gun barrel," as well as in the other tanks, is drawn off from time to time.

A gun barrel heater for treating oil-water emulsions commonly termed "BS" has been described in the *Petroleum Engineer*, p. 55, December, 1932. Its construction is simple. The dome of the boiler is connected to a coil in the gun barrel and a return line from the coil is connected to the side of the boiler, forming a closed-steam circulation system. The coil is above the boiler. A lubricator is welded into the side of the dome for adding make-up water. The normal working water level of the boiler is half way up in the dome. Water is drawn from the gun barrel until the oil level is below the point where the coil is to be installed. By installing the coil high in the gun barrel no heat is lost from the siphon. The thermal efficiency is high (65 per cent). The metal that comes into contact with the salt water is the coil in the gun barrel, which may be replaced at a small cost. The boiler heater easily handles about 5 barrels per 24 hours per square foot of heating surface.

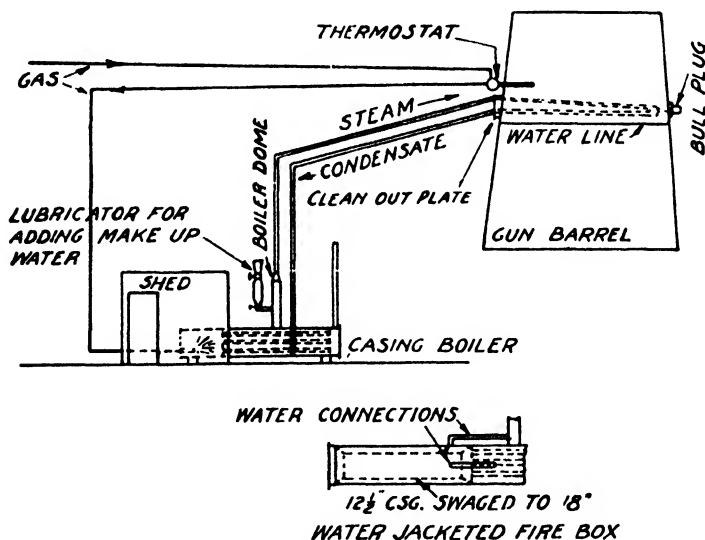


FIG. 1. General Sketch Showing Field Heating Plant for Treating Emulsions.

Ross (Great Lakes Pipe Line Co.⁴⁴³) considers the "gun barrel" tanks efficient in treating cut oil. This is a three-way treatment, i.e., heat, wash and chemical.

The gun barrel is shown in Fig. 1. For two-thirds of its height the gun barrel is filled with salt water, maintained at a definite temperature by means of steam coils set above the tank floor. As the oil descends the boot, the cut oil rises through the heated mass of salt water, and is heated and washed thereby. The pipe-line oil from which the emulsion has

been separated rises to the top of the fluid level in the gun barrel. The "BS" is broken into its two component parts of oil and water, while the latter stays behind in the wash; the oil joins the free oil. Surplus water is bled off the gun barrel by an automatic siphon (Fig. 2).

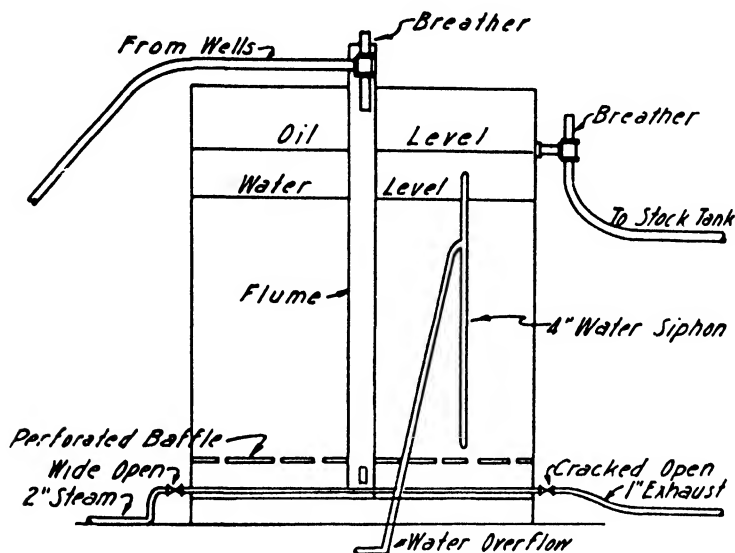


FIG. 2. Gun-barrel Tank.

In treating emulsions with steam, it is customary to heat the incoming cold emulsion with the outgoing heat-treated oil. Devices for this procedure are known as heat exchangers, and assume various forms. The amount of hot oil necessary to heat the cold emulsion is calculated according to the formula: $HST = cst$, where H = weight of the hot oil; S = specific heat of the emulsion; T = difference in temperature between the hot oil and the emulsion at the beginning of the dehydration process; c = weight of the emulsion; s = specific heat of the hot oil, and t = difference in temperature between the hot oil and the emulsion at the end of the dehydration process. Therefore, the weight of the hot oil required to heat the weight of the (cold) emulsion through temperature in degrees F is: cst/ST .³⁸⁴ The heat lost by radiation is a negligible factor in this calculation, for it is assumed that the amount of heat lost by the hot oil is equal to the amount gained by the (cold) emulsion.

It has been recognized by research specialists that there are definite practical requirements that must be met in case of heaters: (1) a demulsifying heater must be assembled and taken apart easily, be light, and readily moved; (2) its throughput must be readily increased at will; (3) it must be efficient for different methods of removing water; (4) it must consist of a limited number of castings.

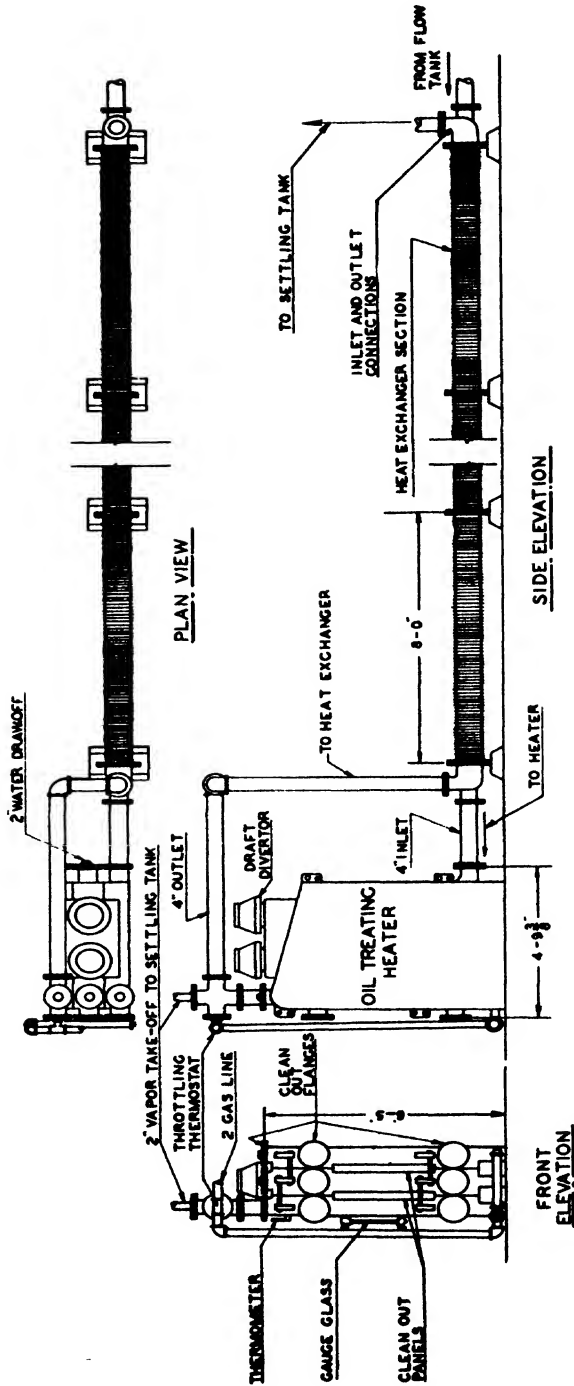


Fig. 3. Typical Assembly of National Oil Treating Heater with Heat Exchanger.

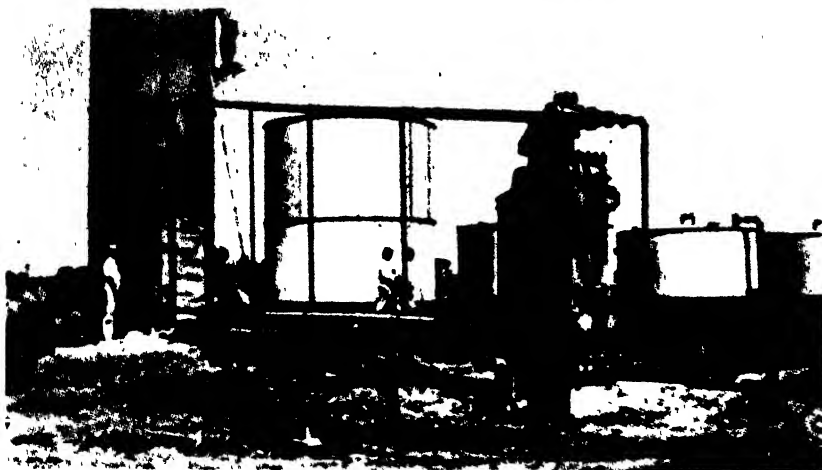


FIG. 4. Cast-iron Sectional Heater Installation in Van Pool, Van Zandt County, Texas.

A special cast-iron heater and heat exchanger lowering the cost of treating oil emulsions is described and discussed by Hunter²⁴⁸ (Fig. 3).

The new heater can be used equally well for direct treatment by passage of cut oil through it, for indirect treatment as a heater for salt water, or as a heater for oil or water as an auxiliary to any other process of treatment. Fig. 4 shows a cast-iron sectional heater installation in

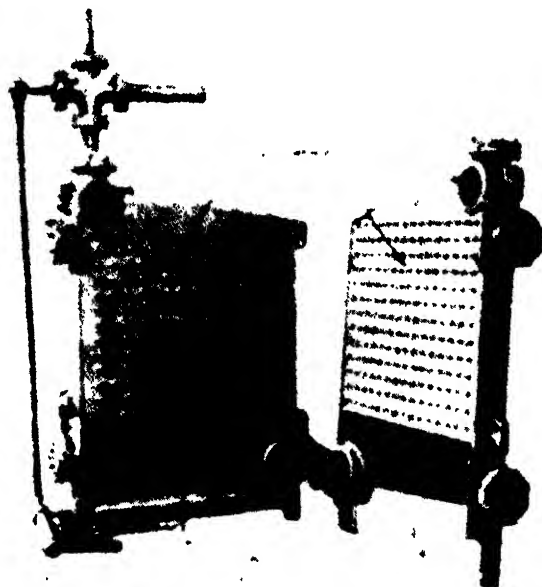


FIG. 5.
Inner View of
National Oil-treat-
ing Heater.

Van Pool, Van Zandt County, Texas, and Fig. 5 an inner view of National oil-treating heater, the latter showing how the sections fit together. The knobs and ribs are extended surfaces to increase heat absorption. The flanged opening at the front and rear, top and bottom of each section permit cleaning of the inside walls. The cut oil enters through one of the rear bottom openings and rises in the several sections. These sections are made wide and deep to cause low flow velocity and more thorough separation. They are smooth on the interior to facilitate cleaning. Discharge to the settling tank is from the top. Best results are obtained by causing the cut oil to percolate through a volume of hot water; the water drain is regulated to maintain a certain level in the heater. This unit is said to show a thermal efficiency of about 80 per cent, and is intended for use where the cost of gas makes fuel economy important. Heat exchangers serve the double purpose of conserving fuel and of controlling loss of light fractions by evaporation. The heat exchanger in the typical assembly for direct treatment serves to connect tanks and heater, replacing two separate lines of pipe. An innovation in this new equipment by the National Radiator Corporation of Johnstown, Pa., is its construction in gray cast iron throughout. It is claimed to be corrosion-resistant and consequently the heater and exchange sections give years of service. The capacities of these heaters range from about 10 to 90 barrels of fluid handled per hour.

The *News Edition*²⁴⁸ of *Industrial and Engineering Chemistry* emphasizes that the new heater is efficient in demulsifying petroleum on widely different methods of removing water, regardless of whether hot oil or hot water is used. It operates on waste gas produced by the wells.

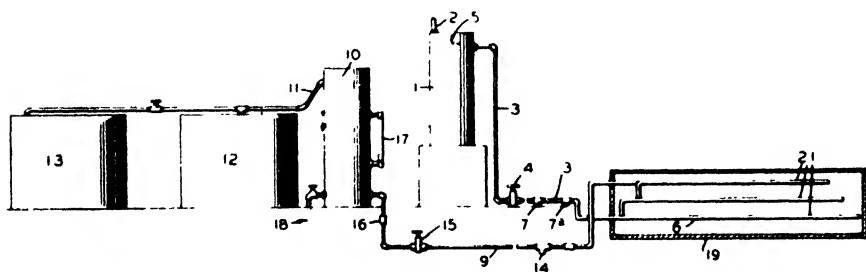


FIG. 6.

The Texas Pacific Coal & Oil Co.⁵¹¹ patented a processing apparatus for the thermal demulsification of pipe-line oil or emulsified crudes. As shown in Fig. 6, the emulsified crude flows from the well to flow tank (1) through pipe (2). The oil then flows by gravity through line (3) fitted with gate valve (4). Flow is maintained without pumping. Float valve (5) controls the flow by maintaining the necessary static head. Line (3) leads through check valve (7) and union (7a) to heater (6) in which the oil is heated to not over 140° F and from which it flows through insulated pipe (9) to separator tank (10) and then through line (11) to

storage tanks (12) and (13). Pipe (9) has a gate valve (15) and check valve (14) and is connected by union (16) to tank (10). From this tank the water level is indicated by gage (17) and water is withdrawn at (18).

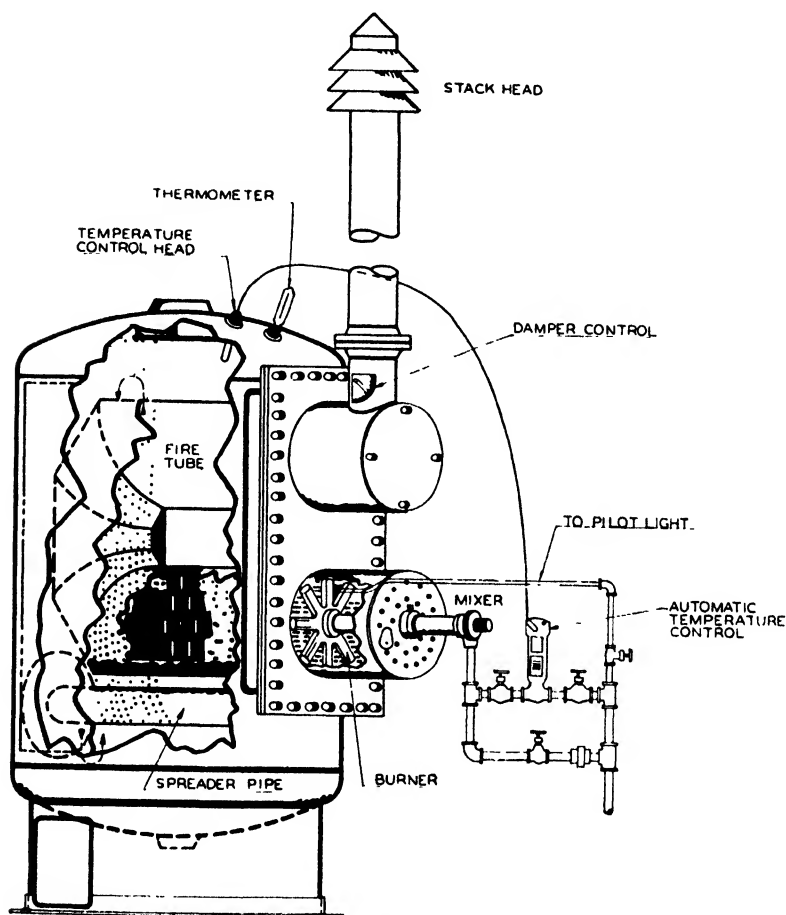


FIG. 7. Diagram of Single Fire-tube Vertical Emulsion Heater.

An efficient type of vertical heater is shown in Fig. 7. The shell of the heater is made of heavy steel plate with seams welded inside and outside. The fire tube is constructed of $\frac{1}{4}$ -inch steel plate and equipped with draft and damper controls. An inlet spreader distributes the incoming fluids evenly; a shield or baffle at the outlet prevents the fluids from channeling through the heater. A flanged clean-out manhole gives access to the lower part of the heater for cleaning, repairing, or replacing of the fire tube or spreader. Each unit is equipped with a thermostat. The operation and maintenance of the vertical heaters is more economical than that of boiler heaters and show savings in fuel. The heaters vary

in size from 4 by 6½ to 8 by 7½ ft. and have capacities from 100-500, 300-1000 and 500-2000 barrels per day. The capacities vary with the heating temperature required, ratio of oil to water, paraffin content, gas volume, and gravity of oil. The maximum thermal efficiency ranges from 60 to 65 per cent.

Heat Dehydration by Distillation

Heat dehydration with simultaneous distillation in a shell still is not feasible with emulsions of high water content. With emulsions of moderate water content, the principal difficulty is to combat the tendency to foam and to boil over. All new installations are able to effect dehydration except those dealing with the separation of very tenacious emulsions. Tube-still distillation allows dehydration of oils with a high water content.

Dvorkovicz ¹²¹ reports the distillation of oils containing 25 to 30 per cent of water by heating in a tube-still and spraying the oil emulsion in a finely divided form in a separator through which superheated steam is passed. Further, the emulsion rises through water heated to 90° C and separates. Allan,⁴ in distilling oils with high water content at 420° F, uses a container consisting of an expansion drum for vapors, two spiral tubes in the vapor space through which the oil is pumped by heating, and an expansion chamber where the entering oil is sprayed downward. Water and light fractions evaporate, and the heavy material flows back over one of the plates into the container.

Wikner ⁶³⁶ reports a fractional dehydration-distillation method. Hydrocarbon emulsions are heated primarily, though not necessarily, to drive off part of the water, and are then passed directly into the still. The distillation process involves delivery of the liquid into a closed container at such a rate that it stands at a constant level, slightly above the inlet, vaporization of water by heat in a zone between the level of the liquid and the outlet, and heating of the bulk of the liquid by the water vapors driven off. Tar is heated by the returned vapors resulting from distillation. Rütgerswerke ⁴⁴⁶ claim that separation of tar from water is effected by the use of a convenient distillation arrangement in which heating takes place from top to bottom, the steam space of the retort being heated first and the liquid space secondly. Floating water, emulsified water and chemically-combined water are separated successively from the tar or oil so treated.

Graaf ¹⁸⁵ heated crude petroleum with fresh water in a container fitted with a condenser until drops of water passed over, when heating was discontinued. After standing, water and other impurities were run off and the petroleum distilled as usual. When the distillation method of removing water from petroleum is applied to petroleum-containing constituents boiling at a temperature lower than 212° F, they are distilled off and condensed. Ordinarily, heat of condensation is lost. Neill ⁸⁶¹ recommends retaining the heat by using multiple-effect evaporators, as well as by distillation under diminished pressure, so that the temperature

for the conversion of water into steam is considerably lowered, Not more than 2 per cent of water-containing emulsions can be taken care of in an ordinary still in which the coil has a 15 to 30 per cent water capacity; a pressure of 20 lbs is maintained on the still to prevent foaming.⁴⁴ Retention of heat in the evaporating chamber may be accomplished by means of conical spreaders in the evaporators. In this case all oil is forced to run down the inside surface of the shell heated on the outside by the escaping flue gases.

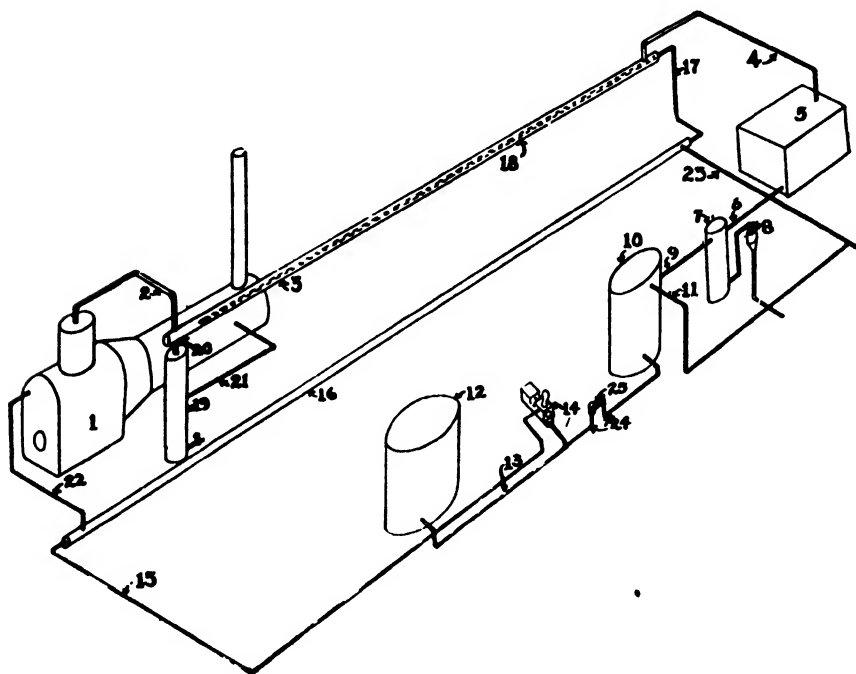


FIG. 8. Diagram of Plant Used to Recover Dry Oil from Tank Bottoms.

Tight emulsions are usually treated at high temperatures over a long period of time, which often results in explosive boiling in the still and foaming over of the contents. Davidson's¹⁰³ device eliminates foaming of tar and similar substances during distillation by contacting foam with a hot surface, whereby the foam, which contains a considerable amount of water, is broken up immediately and subsides. In this process, there is a momentary condensation of a part of the heating fluid, with the result that less heat is conveyed to the heating source. Dehydration is retarded until foaming subsides. The hot surface is maintained at a temperature above that of the foam by circulation of steam or other heat producers through suitable channels in the heating surface.

An apparatus¹⁰³ for distilling emulsions which froth when heated comprises a container with an inlet pipe near the bottom and an outlet

pipe for maintaining a predetermined liquid level within the container. Above the liquid level a vapor space is maintained within which are numerous froth-disintegrating heating tubes. The heating tubes are connected directly to one of the froth-disintegrating tubes. The latter have no connection within the container, but are connected with a common inlet header exterior to the container. The heated liquid is discharged from each of the immersed tubes through a common outlet header.

L. E. Smith⁴⁸¹ describes a method for recovering oil from any tank bottom accumulation regardless of water content, percentage of solid matter, age, source or manner of formation, which was developed by J. N. Hunter of the Gulf Pipe Line Co. in mid-continent. The equipment used in the Hunter method is shown in Fig. 8 in which (1) is the still; (2) the vapor line from the still to the evaporator; (3) the evaporator (made of 6-8-inch pipe, about 40 feet long, in which the diluted emulsion contacts hot vapors from the still and the water is evaporated); (4) is a vapor line from the evaporator to the condenser for carrying water and light oil vapors; (5) a condenser for condensing the cooled vapors; (6) a line from the condenser to the water separator; (7) a water separator (water settles to and overflows from the bottom while the light oil overflows from the top); (8) a water overflow pipe; (9) an oil overflow line; (10) a light-oil storage tank providing a supply for diluting the raw emulsion; (11) an overflow pipe through which the surplus light oil passes to permanent storage; (12) a supply tank holding raw emulsion to be dehydrated; (13) a line carrying emulsion from the supply tank to the charging pump; (14) a steam pump for charging the mixture of emulsion and light oil to the evaporator; (15) a line connecting the charging pump with the inside pass of the heat exchanger; (16) a heat exchanger in which hot dry oil gives up a portion of its heat to the charged mixture; (17) a line conveying the hot mixture from the heat exchanger to the evaporator; (18) a perforated pipe from which the hot mixture of emulsion and light oil is sprayed into the hot vapors in the evaporator; (19) a settling tank to collect heavy solids before the dry oil passes to the still; (20) a pipe connecting the evaporator with the settling tank; (21) a pipe from the settling tank to the still; (22) an overflow pipe for continuous and automatic discharge of dry oil from the still; (23) a pipe conveying the dry, cool oil from the plant to permanent storage; (24) a line carrying light-oil distillate from the light-oil storage tank to the charging pump; (25) a regulating valve controlling the amount of light-oil distillate being mixed with the crude emulsion.

The advantage of this method is application of heat inside the container in which water is evaporating. When heat is applied from the outside, heavy scale quickly forms and forces frequent shutdowns for cleaning still or boiler. The temperature used is above 212° F. In an emulsion containing very small droplets, the temperature may have to reach 300° F.

A method of breaking emulsions, adapted to the treatment of heavy oils, is the so-called "topping plant." The general method is to pass the

oil through pipe stills in which it is heated to 350-500° F. From the pipe still the oil passes into settling towers in which the heavy portions of the oil settle out while the more volatile portions pass over. After passing through condensers the water can be separated readily from the light oils. A process suitable for dehydration by heat of crude petroleum containing natural brines composed of chlorides, sulfates and carbonates of sodium, magnesium and calcium, as well as sand and other similar impurities, has been described by Allinson.⁵ In this process the crude is forced at a very rapid rate through heated coils, and is heated to a temperature at which a considerable amount of water and salt are set free from the oil. The heated mixture passes to a separating tank in which the speed of the liquids is greatly reduced so that the sediment settles out and is removed. The clarified oil is re-passed at a higher speed through a second set of heated coils in which it is heated to a temperature above the boiling point of water. From this final heating the mixture is sprayed directly into a vapor separating tower in which the oil and water are finely divided, and a part of the water and volatile constituents of the oil are vaporized and condensed. Finally the oil, substantially free from water, enters a battery of stills wherein it is subjected to fractional distillation. The hot residue from the distillate is used to heat the crude oil passing to the vapor separating tower.

Dehydration by Indirect Heat Treatment

Heat treatment for the dehydration of emulsions is often carried out in an indirect way by using heated surfaces. The water particles tend to adhere to the surfaces of the metal and to absorb heat therefrom, becoming heated above the boiling point, although surrounded by oil which is very much below the boiling point. As a result, the small water globules are converted into steam, leaving the dissolved matter in the form of a solid adhering to the metal surface. Cameron⁷⁹ overcomes the difficulty by evaporating the water without allowing it to come into contact with heated metallic surfaces. The dehydrated oil circulates around a closed ring containing a heater and a vaporizing chamber. The emulsion is injected into the ring after the dehydrated oil leaves the heater, the water vapor being withdrawn from the vaporizing chamber. The oil leaves the heater at a temperature exceeding the boiling point of water and at the pressure of the vaporizing chamber. Jaworski²⁵⁵ describes an apparatus for dehydrating tar, adapted for circulating tar in such a manner that it is projected upward against a transverse separating plate or baffle. The tar is heated by a heating coil. The temperature used is 50-60°, which is sufficient to reduce the specific gravity, but not sufficient to boil the water. The heater has a conical upper portion and a central outlet aperture. Wright's⁶⁵⁴ dehydration equipment is a combination of a container with a cast-iron housing which has a rotating plate, against which the emulsion is forced. According to Mandutz and Wohlleben,³¹⁹ the emulsion to be dehydrated passes over alternately arranged heated plates placed in sloping positions in a closed container.

Soc. An. des Pétr. Huilles et Derivés⁴⁸⁵ patented the application of heat by using parabolic reflecting surfaces in the focal points of which finely divided oil circulates. Marx³²⁴ claimed a dehydration process based on slow circulation over a row of partitions. Gehrke¹⁷⁵ removed water from oils settled from condensates by heating the chamber (used for collecting the separated oil) from the outside by means of a spiral tube. Kubiersky²⁸² passes the oil to be dehydrated in a thin layer over strongly heated plates, arranged vertically or almost vertically, and claims that the water evaporates completely.

Hammond²¹¹ and Richardson⁴²⁸ report an apparatus for dehydrating coal-tar and mineral oil. In the upper part of a still is placed a preheater containing a series of overlapping baffle plates arranged stepwise. The crude oil is led onto the uppermost plate and flows down the series. The light oils and water are vaporized and removed through an outlet pipe. From the lowest step the tar or oil to be dehydrated passes into the still proper, where it is drawn off through a suitable opening. Vapors given off from the still pass between the baffle plates of the preheater, which serves also as a fractionating column. The heavier portions produced by local overheating return into the still. Smith⁴⁸⁰ separates the oil phase from the water in an emulsion by bringing it into contact with a solid object heated above 100°. Prutzmann⁴¹⁸ uses steam coils at the bottom of a retort placed directly above oil coils which are provided with openings, the oil being sprayed upon the steam coils. According to Wilke,⁶³⁹ the crude oil runs from an overheated container onto a circular plate heated to the requisite temperature by a lead or oil bath. The oil flows into a trough-shaped container, deposits there the remainder of the salt, and is run off by an overflow pipe into a suitable receiver. The steam and other vapors pass from the top into a condenser. To prevent the gases from flowing back to the apparatus, the inlet and overflow pipes are provided with suitable traps. The salt deposited must be removed at intervals from the plate, as well as from the settling container.

Glossop, Bradley and Willisdon¹⁸³ dehydrate tar by allowing it to stream as a cascade over surfaces inclined toward each other. The vapors formed penetrate the tar. According to Dyer,¹²² the oil to be dehydrated flows in a thin layer over heated surfaces in a closed container and enters without cooling after the removal of the lighter, vaporized portions. The oil enters a second closed container, where it is again made to flow in a circuit over heated surfaces at a temperature and pressure higher or lower than that in the first container. External heating is used for one of the containers, and the vapors generated therein are conducted through the other container heating the oil. In each container the oil is agitated during heating.

Wagner⁶¹⁷ breaks petroleum emulsions by leading them over zig-zag inclined plates into an arrangement heated with steam. Water droplets are thus separated, and the oil and water are drawn off separately from the bottom. Fearis¹⁵⁴ leads emulsions through kettles closed at the top and bottom and containing a large number of vertical tubes through

which superheated vapor is passed. deCamp⁸⁰ dehydrates Southern California crude petroleum containing water and a considerable proportion of an asphaltic substance and a brown granular substance (the emulsifying salt) by spreading it over a heated surface in the open air; it moves under the action of gravity. The temperature is kept high enough so that water evaporates rapidly; the oil is thus purified while passing over the surface, without an appreciable loss in the lighter fractions. The presence of water permits application of a higher temperature (302° F) than that at which oil would actually boil, the heat being taken up rapidly by the water and carried off as steam, which prevents detrimental volatilization of the oil. Lindsay³⁰³ heats the crude oil to be dehydrated to 150° F in a tube placed in an oven, and then allows it to enter an open pan placed in the upper part of the oven; the oil expanding there comes into contact with the air. A simultaneous separation of water by gravity takes place. The apparatus consists of a furnace and oil-conducting pipes in the furnace underneath the shallow pan. Traps are arranged to extend downward into the fire-box at regular intervals along the pan. Air is admitted across the pan.

A number of patents describe the use of metallic baths in dehydration processes. Duckham¹¹⁸ patented a scraping arrangement above a metal bath. Mette³⁴¹ proposed a container partially filled with a metal bath having a chamber system provided with alternately perforated metal sheets, the flow of the oil through the system being regulated. The temperature used for dehydration in such a chamber system is about 380°. Thermal Industrial and Chemical Research Co., Ltd.⁵¹² passes the starting material through a tube placed in a metallic bath, the temperature of the bath being maintained at the critical point of the highest-boiling distillate to be obtained, cracking of the liquid being thereby avoided. Morgan³⁵⁰ uses a drum dipped into molten metal.

Heated gases or air are often applied for heating an oil to be dehydrated. Seymour's⁴⁶² method of precipitating water and other impurities present in petroleum oil consists essentially in heating natural gas and passing the heated gas through the oil. Kelley's²⁶⁵ method involves circulation of oil in a gradually narrowing stream and heating it with flue gases. Swarteslander's invention relates to the dehydration of mineral oils, ascending gases being used to heat the crude oil. The apparatus for heating the crude oil consists of a tank, a coil, pipes connecting the coil with the tank, an oven enclosing the coil, gas pipes, a gas reservoir located entirely above the level of the tank with which pipes are connected, and a gas feed pipe leading from the reservoir to a burner.

The average treating plant for water-in-oil emulsions consists of the following major units: (1) heater, thermostatically controlled, (2) wash tank, and (3) settling tank. The method of connecting these units varies from one company to another. Some companies pump the fluid produced from the wells through the heater to the wash tank and from the tank it flows by gravity through the settling tank to the stock tanks. Other companies pump the fluid directly into the wash tank, and a heater

is used which keeps the water in the wash tank hot by a thermosyphon action.

In this case the heater is the barrel of an oil-field type of steam boiler that has been cut from the fire-box of the boiler, and a steel plate with a door welded on where the barrel had joined the original fire-box. Connections from the bottom of the wash tank are led into the bottom of the heater, and the discharge of the heater is connected to the wash tank at the water-oil level.

Upon heating, the water naturally rises, and in so doing is discharged into the tank, being replaced in the heater by water from the bottom of the wash tank. Heat may be applied to the emulsified oil by steam coils in the bottom of the wash tank.²⁵²

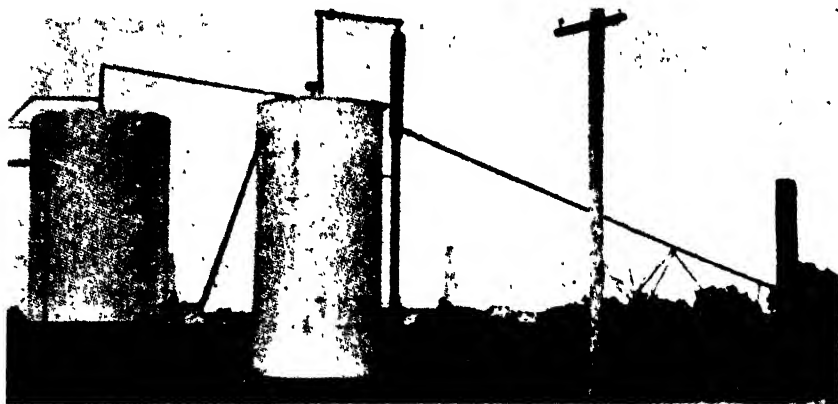


FIG. 9. Treating Plant Composed of Boiler, Heater, Wash Tank, and Settling Tank, Seminole Area.

W. Woelflin⁶⁴⁸ considers the losses in gravity and volume when handling hot crude oil. Depending on the temperature of the oil and the manner in which it is handled after leaving the dehydrator, there is a greater or smaller loss. If the oil passes through a heat exchanger or cooling tower and then goes into the bottom of a vapor-tight tank, there is practically no loss of gravity or volume. If the oil enters the tank through an ell at the top of an open manhole, maximum loss takes place. It is suggested that oil from the dehydrators should always enter the stock tanks at the bottom, especially when oils lighter than 20° A.P.I. are handled. Heat exchangers or cooling towers minimize gravity losses and should be used on oils lighter than 25° A.P.I. in order to cool the oil to 140° F or below, depending on its gravity. When oil enters the bottom of the tank at a temperature of 140° F or below, depending on the gravity of the oil, the gravity loss should not be over 0.5° A.P.I. With vapor-tight tanks, in addition to the conditions mentioned above, the gravity loss can be reduced to 0.1-0.3° A.P.I. or less.

Heat Combined with Mechanical Treatment

It is a fact that under certain conditions mechanical agitation may induce coagulation of an emulsion system by effecting an intermittent displacement of newly formed surfaces. This has led to the idea of applying agitation simultaneously with heat treatment for breaking emulsions. The Asiatic Petroleum Co.¹³ patented an apparatus consisting of a make-up pump, a circulating pump, a vaporizing chamber and a heater. The oil to be dehydrated is delivered by the pump through a pipe into the top of a vaporizing chamber in which the oil falls on a spreader covering the end of a vapor outlet pipe, the end of which is perforated. A constant circulation of oil is effected by the pump. The oil is heated in the heater above the boiling point of water. Kelley²⁶⁵ uses a simple system for the separation of water, *e.g.*, the oil is passed from the well to a heating tank of considerable size. The crude oil is directed into the heating apparatus in such a manner that a column of oil of relatively small transverse area and of indeterminate length is caused to move when heated. The temperature is less than the boiling point of water and is most efficient when maintained at about 190° F. The apparatus comprises a furnace, and a hot-water drum arranged horizontally in the furnace with an elongated oil passage in the drum. According to Bending's⁴⁶ process, the oil in a finely divided state falls in contact with an ascending current of heated air which is warmer than the oil; the descent of the oil is intercepted by a surface, which causes the oil to splash and break up. The oil is continuously collected in the bottom part, drawn off from the upper part, and again subjected to separation and exposure to heated air until it is dehydrated. Spiegler⁴⁹⁰ brings about dehydration by passing the oil into a container steadily stirred on a vertical axis. On rotation the oil is thrown against the hot surfaces of the container walls.

Mechanical treatment in itself may also assist in resolving emulsions. It is known that some hydrophobic sols, such as copper oxide and goethite, show mechanical coagulation.¹⁶⁵ According to Freundlich and Loebmann¹⁶⁶ and to Deutsch,¹¹⁰ mechanical coagulation occurs at the liquid/gas boundary. That vigorous stirring causes separation of phases, according to Clavel⁸⁶ and Karpinsky,²⁶² is explained by the fact that drops collect at the liquid/air boundary. Freundlich and Loebmann found experimentally that the rate of coagulation increases with the square of the rate of stirring. Coagulation takes place at the surface of the solution where a certain arrangement of particles may exist. Another interpretation was suggested by the electrical conductivity measurements of Lesche.²⁶⁹ The process of coagulation of these systems has been considered to consist of a gradual transition of the hydrolysis product from a hydrophilic to a hydrophobic colloid, the process being irreversible. Mechanical coagulation is carried out, according to Freundlich and Recklinghausen,¹⁶⁷ in a so-called free stirring container. First constructed by these writers, it consists of two parts ground into each other. The lower

part is cylindrical with a wide, ground edge. The bottom of the upper part is perforated with 10-mm holes in the middle. The upper bottom has two narrow holes through which the colloid circulates from the lower part into the upper. Streaming occurs when the liquid is taken by the stirrer and thrown upon the walls of the container, the liquid slipping partially upward and then streaming down at the surface toward the middle. Through the peripheric holes streaming takes place from bottom to top, and through the central hole from the top to the bottom. The action of the stirrer in the first phase of the process consists in a distribution of the heavier liquid in the colloidal solution and then in the adsorption of the small primary particles at the newly formed surfaces.

The principle that an emulsion may be destroyed, as well as formed, by agitation, has been used in many patents. According to Sheppard,⁴⁶⁹ disintegration of an emulsion is formed by slow, continuous shaking, emulsification being accelerated by a single shake. On the other hand, slow shaking, suddenly much accelerated, may cause re-emulsification. Bechold, Dede and Reiners⁴² claimed an optimum of 10 minutes' shaking for emulsions with finely divided solid bodies; rapid shaking should be avoided. Haulon²¹⁸ patented the use of sprayers moving in a horizontal direction and actuated from the outside in a vertical direction. Henneberthe and Goutal²²⁵ claimed an apparatus consisting of horizontal or sloping troughs with a spiral stirring device. According to Higgins,²⁴⁰ a container divided into sections is used. In one section the liquid flows upward and passes over a wall, and in the next section it descends. Free-land¹⁶³ patented a combination of a heating apparatus with separately arranged pipes like concentric castings, connected in a special manner so that they stir the oil.

Palmer³⁷⁰ describes an apparatus for dehydration of hydrocarbon emulsions. It is based on a relatively rapid, short oscillatory motion imparted to a flowing stream of oil containing water in order to effect demulsification. Mangelsdorff³²¹ uses a central stirring device for dehydration. Evans¹⁴⁹ heats oil while it passes stepwise downward. Wright's⁶⁵⁶ process of treating impure petroleum to relieve it of water and impurities involves spraying and atomizing the impure oil against a rotatable baffle, spraying hot water into contact with the atomized oil, agitating the mixture and passing it through a series of vertical chambers where the oil and water separate by gravity, the oil being drawn off. Roberts reports that it is practically impossible to dehydrate the oil by this method and that it is rather an emulsifying scheme.

In the literature there are patents on dehydration by heat also using special separatory equipment. Holford and Harvey²⁴⁵ use an arrangement to separate water from oil consisting of a column with a series of perpendicular baffles and a rotating distributor, which the liquid enters and through which it streams, having so-called reaction surfaces. McArthur³²⁸ uses two independent surfaces sufficiently close to each other to form a capillary opening between them. A water film is formed in the capillary opening and the oil and water mixture is separated.

According to Shaw and Beale,⁴⁶⁸ the liquids are introduced from below into a separation apparatus, coming into contact with one or more horizontal plates forming the upper surface of perforated canals opening into a tube or a receiver for light liquids. The heavy part of the liquid drops down at the edges of the plates.

Brady⁵⁹ conducts the oil into a vertical cylindrical receiver wherein two mechanically operating cut-off valves are placed which function at a definite liquid level. Two plates are fixed in the apparatus, one directly above the upper opening for light oil and gas; above that is a heating system. The improved apparatus takes the place of the conventional gun barrel and settling tanks and performs the functions of settling out sand, venting gas, breaking up the emulsion and continuously withdrawing the separated oil and water during the continuous operation. Hopkins²⁴⁰ uses an apparatus consisting of upper and lower oil chambers provided with heat tubes and connected by a series of open tubes. Oil flows from the bottom to the top and from there to the outside.

Hurdelbrink²⁴⁹ patented a device for constant separation of two immiscible liquids of different specific gravities, both combining to form a continuous stream. The separation space brought into the liquid stream is placed deeper (many times its height) than the inlet of the liquid mixture. The outlet for the lighter liquid is placed as far above the outlet of the heavier liquid as required by the difference in specific gravities.

White's⁶³³ invention relates to an apparatus for separation of liquids of different specific gravities. A separator of this kind comprises a container having an inlet and an outlet. The separator has a part which converges in an upward passage. Upward and downward passages lead from the separation chamber to the outlet of the container. They converge in the direction of the flow.

Pippin⁴¹⁰ proposed an automatic device for separating water from oil, which consists of a cylindrical float chamber with an outlet at its bottom. A valve is carried by the bottom of the float and adapted to the seat on the outlet. There are a great many radially disposed ribs on the vertical walls of the float; the ribs serve to guide the float in a true vertical direction and to prevent it from rotating in the liquid. The tank for separating liquids of different specific gravity has an inlet and an outlet communicating with a main tank. The float valve controlling the outlet is normally raised by liquid of one specific gravity and permitted to descend to close the outlet in a liquid of different specific gravity. The communication casing has a valve normally sealing the outer end of the outlet to prevent formation of a vacuum and consequent sticking of the float valve. A baffle plate located in the tank serves to direct the liquid away from the outlet pipe in its bottom.

Noerdlinger³⁶⁸ uses a separation box with partitions inserted in the direction of the current and extending toward the bottom. The partitions do not reach the bottom entirely, for toward the end of the box the distance from the bottom gradually increases.

The separation of oil from oil-water mixtures may be based on capil-

lary action or surface attraction. McArthur and Maynard's ³²⁹ equipment consists of a separator above which is placed a precipitating and a collecting container for the oil; this is connected with the separator by a descending tube for the oil-water mixture and an ascending tube for the separated oil; the latter simultaneously serves to introduce the mixture. The lower part of the separation container is provided with plates placed in layers one above another so as to form narrow openings which, on account of their form and size, are suitable for the passage of water but which, on the contrary, retain the oil because of capillary or analogous action. The water from tanks containing oil/water mixture may be removed by using this arrangement. From time to time the equipment is cleaned by using water or vapor under pressure to blow through the narrow slits between the plates.

Lozai ³¹¹ dehydrates crude oils, using countercurrent flow. This apparatus is made up of vertical pipes with a heating chamber for heat exchange. Passavant Werke ³⁷⁴ patented a float-controlled valve regulating the influx of the oil. The body and float of the valve are connected at the end of a double-arm lever. The float is in the separation chamber and the valve is in a valve chamber placed between the separating and the sludge chamber.

Peterson ³⁷⁹ introduces the oil-water mixture uniformly and continuously into a relatively heavy or light liquid; the distance of the course is calculated to be sufficient for separation to occur on account of the difference in density. Pink ⁴⁰⁹ dehydrates by using a separator consisting of a rectangular container with swinging partitions operated by means of a floating arrangement, a piston causing the oil valve to close and open. The length of the container is such that distance and time are sufficient to permit settling of the heavy liquid. Ruppert's separator has heating containers placed at various low levels, and an elevated separation tank. Regulation of the liquid level is carried out by an adjustable arrangement or screw plates. Sander ⁴⁵¹ conducts the emulsion through one or more containers, each provided with a syphon. One end of the syphon dips into the liquid, while the other controls the exit of the liquid.

Seiler ⁴⁵⁹ patented an oil separator. Sepulchre ⁴⁶⁰ permits the mass to be dehydrated to rise, while the speed of the heavier liquid is lessened by widening the diameter of the channels which lead the liquid to a discharge line. A tar emulsion separator is described in the Metcalf-Shaw process.³⁴⁰ It is based on the existence of a capillary attraction between liquids and bundles of tubes or rods placed in contact with one another, the surface tension forces characteristic of emulsions being exceeded. Pirbright Co., Ltd.⁴¹¹ claimed that an arrangement comprising long horizontal chambers permits the rising light liquid to enter a general collecting container, this being a settling basin such as those used in gas plants for separating water from gas-tar.

Pravicha and Douillet ⁴¹⁶ patented an improvement of the interior part of the discharge pipe of a separator. They hung a weight in the discharge pipe to increase the weight of the discharge funnel. Sorge ⁴⁸⁶

recommended an apparatus to separate water from emulsions. Sperling⁴⁸⁹ created a space suitable for separating emulsions through the distance of two closely spaced plates, of which one is stationary while the second is kept in motion. Stephens⁵⁰¹ constructed two long horizontal separation chambers between which a collecting container with collecting channels is located.

Teegen⁵⁰⁸ described a collecting container with one or more closed containers having an overflow at fixed heights corresponding to the specific gravity of the lighter liquid to be separated and an adjustable overflow.

Schroeder's invention⁴⁵⁵ relates to a piece of equipment for evaporating and cooling emulsions the working surface of which is formed by the internal surface of a wooden cylindrical drum open in front, and possessing a flange turned inside out to provide a space for taking up the charge. On the side opposite the open end of the drum are placed a centrally located pivot for carrying discharge equipment and a cog-wheel, which is geared to the axis of the discharge equipment and actuates it. Introduction or removal of the cooling water or heat agent into or from the ring space formed by both cylinders takes place through a straight tube inside of another tube. The ring chamber is provided with openings to give an outlet for cooling water or the heat agent.

Schmidt's⁴⁵² separator is distinguished by narrow chambers provided with partitions arranged in a zig-zag manner so that corresponding channels are formed. The partitions are adjusted to the lower side of a cap forming the cover of a pyramid-shaped body and provided with a funnel. Dempster¹⁰⁸ makes use of an overflow cup for dehydrating tar. The cup is attached to a pipe which is moving up and down. Daughdrill¹⁰² patented as a separator a combination of a container with steam nozzles. Dodge's¹¹⁶ container has a float. Debaecker¹⁰⁴ claims a container with a vertical pipe inserted into the liquid; it is open at the rim and ends at the bottom in an open funnel. The mouth of the funnel is below the level of the heavy liquid ascending in the container.

Fahl¹⁵⁰ claims a separation container open at the top and built into a collecting container at or near the bottom. The collecting container is provided with a syphon discharge pipe so that only when a certain pressure is reached does the heavy liquid from the filled separating container pass over into the collecting container and the lighter liquid pass over first to the upper rim of the separating container and then into the collecting container. Esterer¹⁴⁸ patented an arrangement for the discharge of the impurities collected during the dehydration treatment. Stair-like, rectangularly bent plates, directed downward, are located in a descending housing, so that there is a long opening between every two plates. Two or more housings may be operated in series; two or more stairs formed by plates are built with a corresponding number of openings.

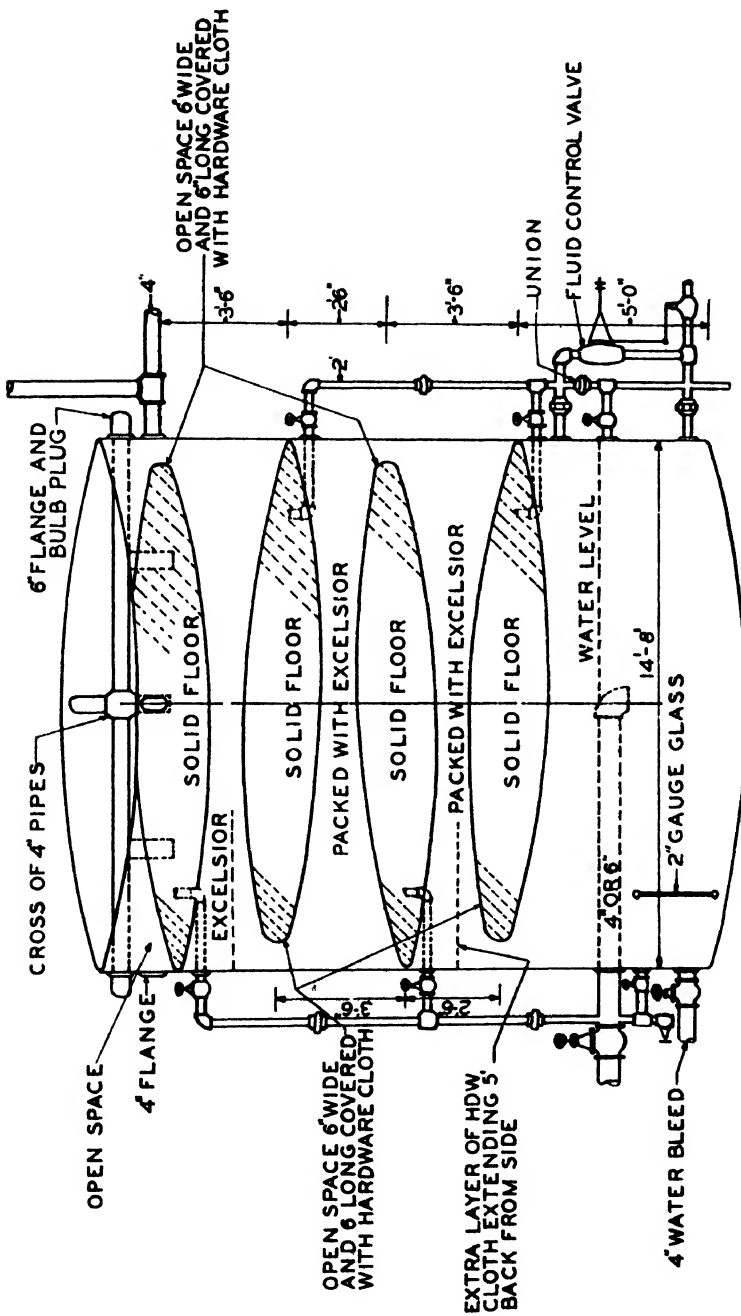
T. Moscicki³⁵⁵ effects dehydration of a natural petroleum emulsion by introducing it tangentially in a continuous stream at high velocity into a heating chamber below the surface of a body of an emulsion maintained in the chamber. The emulsion is slowly drawn from a point

slightly below the surface of this body of emulsion and then passed to a separator, where water and oil are separated. Tank and baffle apparatus for breaking petroleum emulsions by passing them upward through water is described in structural and operative detail by Bays.⁴⁰⁸

White⁶³² uses inclined baffle plates by which the flow of the liquid is reduced. Concentric separation chambers are enclosed in a larger container. The innermost oil separation chamber is made narrow toward the oil outlet by the use of a cylindrical partition and an attached container with a cylindrical bottom. Meston's³³⁹ improvements of a separator are directed to a container having an emulsion-receiving compartment at one end and a means of discharging water at the other end; there is also a series of intermediate baffles disposed transversely across the tank and extending vertically only part way. Filming of the oil occurs upon these plates, allowing the heavier liquid to flow continuously. The liquid rising over the baffles falls by gravity into the succeeding compartments.

Green and Unthank¹⁸⁸ separate oil from water by allowing water containing the oil to flow under pressure very slowly through a tank filled with pure water, the upper part of which is divided into many small streams passing through a perforated arrangement enabling the oil to rise upward, while the water is drawn off through an outlet tube underneath. American Air Filter Co.⁹ separates emulsions by using an arrangement containing a number of distorted shovels of equal length, spaced regularly, between which the emulsion flows. An apparatus for dehydrating petroleum oil emulsions by heating was proposed by Turner.⁶⁰⁹ A heated tank for separating oil and water from oil-field emulsions was patented by McMurray.³³⁶ A high-capacity emulsion treater has been installed in a refinery at Waterloo, Arkansas.⁴³² Smith⁴⁸² describes this low-cost method of treating crude having a water content of 15 to 45 per cent. First chemicals are added to the crude; it is then heated with gas fuel to 210-220° F; 60 per cent of water is separated in this phase of the process, the remainder being flashed off by heating to 240° F in a second heater unit. The first section of the heater is kept full of water so that the entering emulsion percolates through it. The operating cost averages two and three-tenths cents per barrel of treated oil compared with eight to twelve cents for other types of treaters. In his emulsion breaker, Raynk⁴²⁵ passes the emulsion through the space between tubes 15 meters long and 5 and 3 inches in diameter, arranged concentrically. Steam is passed countercurrent to the emulsion, which flows to a settling tank where the water separates out.

Oil and water may be resolved and separated in some instances without the use of heat. Mechanical dehydration deals with (a) the excelsior and (b) water-knockout systems. Selective wetting was recommended for breaking emulsions. Water may be separated from oil by running an emulsion over excelsior, laths, etc., which have been previously wetted with oil or water, whichever is the internal phase of the emulsion concerned. Similar to this action is the spraying of water down through a tower of oil to remove a water phase, or spraying oil up through a water



layer to remove an internal oil phase. The spray in each case must be relatively coarse in order not to form more fine droplets (Fig. 10).

The excelsior system is based on the principle of preferential wetting; when petroleum emulsion is passed through it, oil and water separate. This system is generally used as an aid to either electrical, chemical, or water-knockout systems.¹ The excelsior tanks, more commonly called "hay tanks," are used also to separate from oil fine particles of water which otherwise would not settle without increasing the amount of chemical or the application of heat. The water-knockout system used in Mexico, West Texas, California, and Arkansas is a system of pipes mechanically designed to provide a suitable receiving reservoir for oil and water that has not undergone a high degree of emulsification. A small excelsior tank between the well-head and the knockout system adds to the efficiency of separation. The device used is the water-knock-out trap. The cut crude coming from the well under well pressure flows through the water trap, where it encounters a back-pressure imposed by

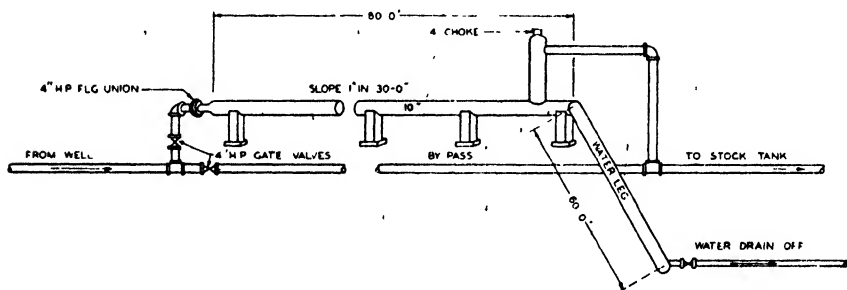


FIG. 11. Type of Water Knock-out Trap Used in West Texas.

the choke. The combination of two opposed pressures and reduced velocity causes the emulsion to break up into its components; and because of its lighter gravity the oil passes through the bean, while the water falls back to a lower level, concentrating in the water leg. The accumulated water is drawn off by a valve or an automatic device. Water traps or "water-knockouts" were used widely until recently, as stated by Curran.⁹⁸ They are not a method of treating, but rather preventive in function, separating the water before it reaches the choke, and allowing clean oil to pass without cutting.

Several successful methods are used for the separation of large quantities of water produced with oil in some West Texas fields.²²³ Among these are the water-trap, hay-tank and gun barrel, gun barrel and settling tank. In the Hendricks oil field the most economical proved to be the water-trap. This trap is installed at wells having considerable well-head pressure and producing large volumes of free water, and where the percentage of cut oil is low. The water and oil are separated under pressure before passing the flow bean and the percentage of emulsion at the flow

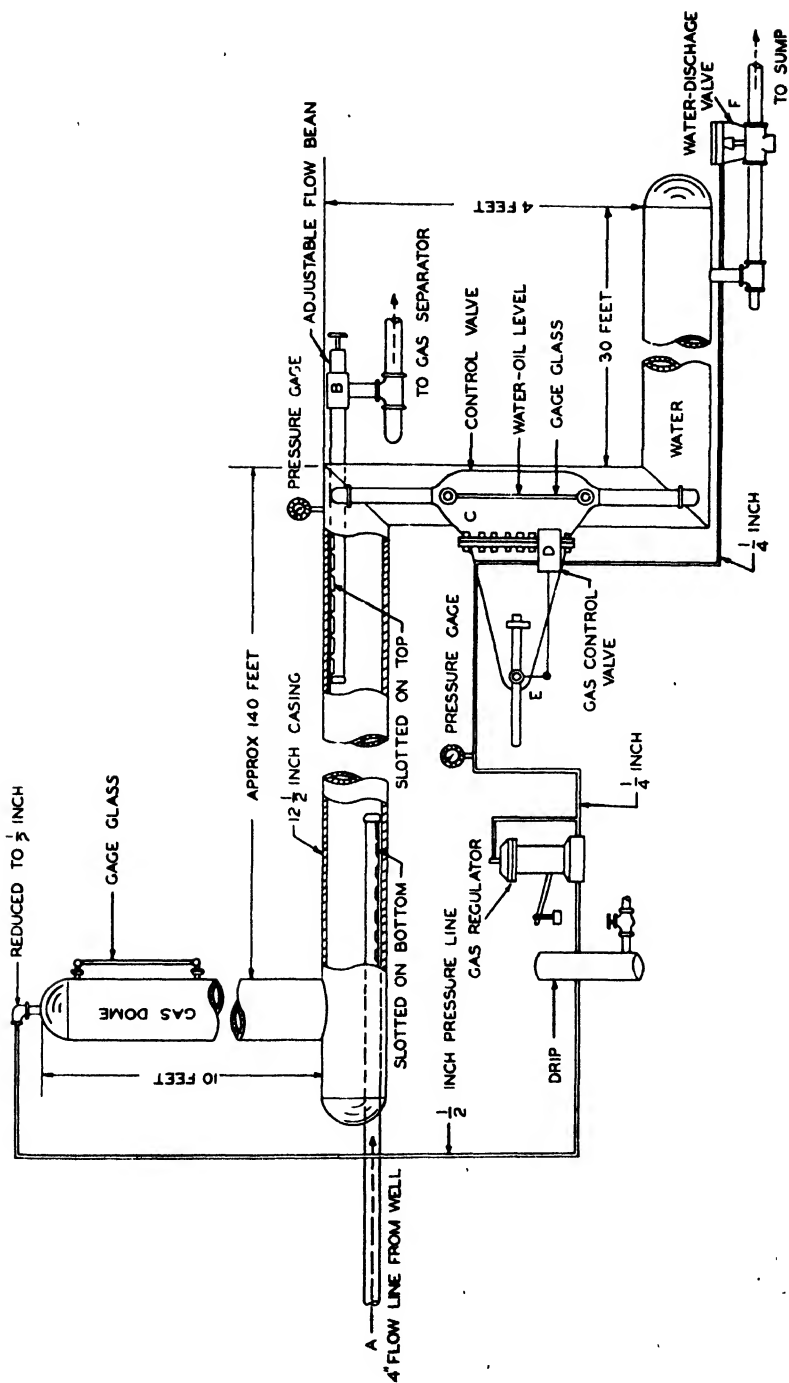


FIG. 12.

bean is reduced to a minimum. This trap is shown in Fig. 11.* The oil, gas and water flow to the trap directly from the well. The fluid enters the trap at the bottom. The fluid velocity is reduced about 9 times when expanded from a 4-inch flow line into the 12-inch trap. As a result of the reduction in velocity, the water settles at the bottom of the trap. Oil and gas collect at the top of the trap and are withdrawn through an adjustable flow bean, *B*, to the oil and gas separator. The trap is equipped with valve, *C*, controlling the liquid level, with a gas valve, *D*, and the water-discharge valve, *F*. When the amount of water in the trap exceeds the adjusted level, the float valve rises, the connecting levers, *E*, open the actuating gas valve, *D*, and the gas pressure on the diaphragm of the water-discharge valve, *F*, is exhausted to a point where the water-discharge valve opens and allows the water to escape (Fig. 12).

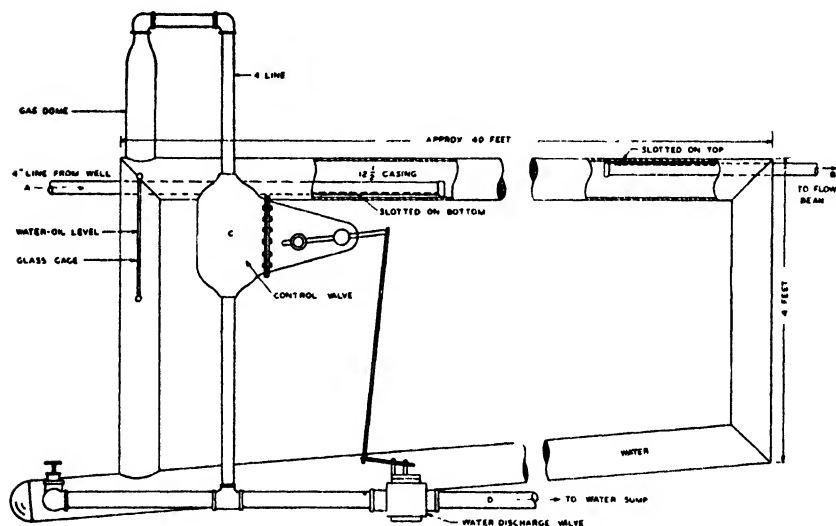


FIG. 13.

In Arkansas, Texas, and California emulsification at the beans of certain flowing wells has been reduced by passing the discharge from the well through a "squeeze trap" in which the free water, oil and gas are separated before they reach the flow bean. Separation in this water trap is accomplished by the reduced fluid velocity and the difference in specific gravity of the oil, gas, and water. Heithecker^{223a} described different types of traps used in the West Texas fields (Fig. 13). In the trap after Heithecker oil, gas, and water flow directly from the well through a 4-inch line to the trap. The line extends about 5 feet into the trap and is slotted on the bottom so that the fluid enters the trap from the bottom of the flow line. The end of the pipe is plugged. Expansion

* W. A. Ross, *Petr. Eng.*, p. 53, March, 1930.

of the fluid from a 4-inch pipe into a 12½-inch trap reduces its velocity greatly, permitting the water to settle to the bottom of the trap. The oil and gas collect at the top of the trap and are discharged through an adjustable flow bean in the outlet line. The float-operated liquid-level, *C*, is adjusted so that the water level in the trap is held midway between the upward and downward movement of the float. The float is operated by water. As the float moves upward or downward, the water-discharge valve is opened or closed mechanically by connecting levers. The trap discharges a continuous stream of water. The advantages of the water-trap are that it separates the oil and water before the oil and gas pass through the flow bean; this eliminates the agitation and emulsification of the oil and water by gas that would otherwise take place. The water and oil are separated under trap pressure, and the oil runs directly from the trap to the stock tanks, reducing to a minimum any agitation that might result in running the oil first through one or more tanks.

Marchant and Wells³²³ carry out simultaneous separation of water and gas from crude oils by conducting them under pressure through a zig-zag passage before they reach a receiver in which the water separates out. Upon release of pressure the gases dissolved in the crude oil separate from it. According to Smith Separator Corporation,⁴⁸³ a mixture of oil, gas and emulsion coming from an oil source in a turbulent stream reaches the middle section of a separation container, provided in the lower third with a heat exchanger. The gases pass to the top and are freed from oil by means of baffle plates; the emulsions are broken in the heat exchanger, and at the same time the undesirable hydrocarbon gases dissolved in the crude oil are removed.

Matheny, Langham, Cloud and Huntington,³²⁵ discussing the separation of gas and oil from gas-oil mixtures, consider that stepwise separation of the gas dissolved in the crude oil works more advantageously because: (1) maintenance of a high back-pressure prolongs the fluidity of an oil by a decrease of the gas-oil ratio; and (2) the specific gravity of the oil is reduced because, by a slow discharge, much less light hydrocarbons are carried away with the gas; therefore, in a subsequent condensation, less oil is lost in the gas line. Gas may be carried away through smaller lines from the well when it is kept under higher pressures.

For separating gas, sand, and water from the oil at the bottom of the well, a separator has been designed by the Miller Combination Boiler and Pump Co. of Sapulpa, Oklahoma.³⁴⁶ This Chancellor separator is a positive gas anchor used below the working barrel at the bottom of the hole; it prevents cutting of the oil by keeping the gas out of the tubing and by pumping the water separately from the oil with perpetual siphon tubes. First a head of water, then a head of oil is pumped through the tubing, keeping worn barrel or cut cups from emulsifying oil and water. The separator has two sand traps, which catch the sand, and keep it out of the working barrel. The separator is 6-18 feet in length, with an outside diameter of 4½ or 4¼ inches. The return siphon tubes are of ¾-inch inside diameter, and the center tubes are 1 inch in diameter.

Heat and Pressure Applied to Dehydration

Dehydration is often carried out commercially by a combination of two or more different treatments or bringing into play various physical factors, such as heat and pressure, or heat and centrifuging, etc. It is highly probable that combined processes chosen with correct considerations act more successfully than single treatments. On the assumption that the decrease in viscosity of an oil on heating promotes coalescence of water particles, experiments have been tried to determine whether additional decrease in the viscosity at higher temperatures, corresponding to increased pressures, would still further accelerate the separation.

Badische Anilin und Soda Fabrik²⁸ treats emulsions with heat, but the crude is heated in closed containers under high pressure and water is blown off this container. Two hundred degrees is considered to be a suitable temperature. Lembcke²⁹⁶ used a vapor chamber and a settling chamber connected by a U-shaped discharge pipe for dehydration. Varying the pressure, a counter-pressure is produced automatically, making the speed of the liquid independent of the pressure in the settling container. Moscicki and Kling³⁵² proposed a method of treating emulsions with heat and under pressure, expecting not only that a decrease of viscosity would occur at higher temperatures, corresponding to the increased pressure which results in separation of phases of the emulsion, but that the time necessary for separation would be shortened also. Heating is carried out in an autoclave. This is a kettle supporting a pressure of 2 to 3 atmospheres maintained for 2 hours, the dehydration being so nearly complete that the final product contains only 0.2 to 0.4 per cent of water.

Edwards'¹³⁶ arrangement for dehydration comprises horizontal pipes and settling compartments. Steam is used as a heating medium and, if desired, it may be worked under increased pressure. Difficulties in the separation of natural heavy emulsions were encountered when small amounts of bituminous particles were present in addition to large quantities of a very fine clay. Moscicki and Kling³⁵⁴ proposed a method of separating water or aqueous solutions from petroleum by heating the emulsions above 100° under at least one atmosphere of excess pressure. Gas or air is compressed in the steam space to prevent boiling, and evaporation. The process is carried out by cooling the steam space. If the gas is forced in before the cooling starts, the separated liquids may be drawn off in a warm state.

Pilat and Piotrowski⁴⁰⁸ favored heat treatment under pressure for breaking crude petroleum emulsions. By heating in closed kettles (capacity of 40,000 kg with steam at 120°-130° and under 3 to 3½ atmospheres' pressure) a practically quantitative separation was accomplished. At 3 atmospheres' pressure only five hours were required. Under higher pressures separation occurred even faster. Primrose⁴¹⁷ applied two receivers for the oil to be dehydrated, and drew the oil from one to heat it under pressure. Then he reduced this pressure and separated the liquid from the vapor which was formed by the pressure decrease. The operation

is repeated as often as necessary to complete the dehydration. The heat of the vapor formed is used simultaneously for preheating the crude material.

Wischetrawski⁶⁴⁴ pointed out that most American emulsions separated under 6 atmospheres' pressure, whereas Grozny emulsions required not more than 3 atmospheres and one hour of heating. Very often the emulsion does not disintegrate by heating under pressure; in this case organic or mineral acids are added, decreasing the viscosity and facilitating resolution of the emulsions. Meredith³³⁸ described a dehydration apparatus consisting of a chamber containing a device for treating an emulsion. The discharge from the dehydrator is controlled. The desired level of oil in the dehydrator is retained at all times, and the escape of gas or vapors from the treated emulsion in the container is prevented. This type of dehydrator, operated without an internal pressure, maintains externally sufficient pressure to facilitate the circulation of the emulsion treated.

Lorenzen³⁰⁹ provides certain improvements in the collecting container of the heat dehydrator. The line leading to the collecting container has an ejector. During the water flow a vacuum is created by the ejector in the closed chamber into which the liquid passing from the discharging to the collecting container is finally transferred. This vacuum may be regulated according to need. The diameter of the overflow line of the liquid from the collecting container may be reduced if overflow holes smaller in diameter toward the bottom are provided in its lower part or at various levels.

Strother's⁵⁰² equipment for dehydration is a combination of a pipe line discharging within a settling tank and an enlarged chamber interposed within the line. The heating means are associated with the chamber, which is entirely filled with oil flowing through it. A check valve is inserted in the pipe line. The check valve opens under the influence of pressure of the oil within the chamber, upon release of pressure of the oil in the pipe line, and is closed by the pressure of the oil passing through the pipe line.

Winkler and Koch⁶⁴³ claimed a process and an apparatus for treating emulsions. The process is regulated to produce any temperature and to operate under any pressure, depending upon the material to be treated. The apparatus consists of a battery of tanks progressively elevated in a series. A predetermined liquid level may be maintained in each tank. Each tank has a spray head, which discharges below the liquid heated therein. A gas supply pipe is connected with the spray head of the first tank. A method of dehydration of petroleum tar is described in German patent 231,222, Feb. 16, 1911. The substance, heated above the critical point, is sprayed under pressure against a turbine wheel through a tube widened at the top; the mass running down in the tube is agitated by a stirrer driven by a turbine, so that the dehydrated product flows down continuously.

The Power Specialty Co.⁴¹⁵ patented a process of heating crude oil

containing water under pressure and leading the oil in a chamber standing under a slight pressure. The water present in the oil evaporates.

Brown⁶⁸ heated a crude oil-water emulsion under a pressure sufficient to prevent foaming, and vaporization of the lighter hydrocarbons. These conditions are maintained until the emulsion breaks down and the water is separated. Jensen's²⁵⁷ process involves heating the crude-oil emulsion to a temperature above the boiling point of water, preferably above 400° F, and then delivering the heated emulsion to an evaporator. All the water and most of the low-boiling fractions are evaporated, the vapor passing to a suitable condenser. After evaporation, the crude oil leaves the evaporator at a temperature about 40° F below that at which it entered, passing either directly to a still or first to a storage tank and then to a still. The water and low-boiling fractions are then removed and the oil delivered to the still at a temperature above 212° F. The hot oil, when passing into the evaporator, is maintained under pressure. The great retardation of distillation caused by foaming in certain oils is prevented by this process.

Burek⁷⁷ described the separation of stable emulsions by the "Metan" method. The apparatus is constructed according to the known principle of emulsion separation by diminishing surface tension as a result of increased heating. The decrease in surface tension takes place at a temperature higher than 100°; therefore an excess pressure originating by heating of both phases, *i.e.*, crude oil and water, is used. The technical equipment in principle consists of a hermetically sealed, evacuated container provided with a manometer and heated either by combustion gases, or directly or indirectly by vapor. In order to avoid loss by evaporation, caused by boiling of water separated at a temperature above 100° and followed by a circulation of water preventing separation, the separation process is conducted intermittently. In this procedure, the container is filled to a certain height and, depending on the quality of the emulsion used, heated to a temperature of 120-140°, whereby the pressure obtained from tensions of both phases amounts to 2-6 atmospheres. The emulsion is kept at the elevated temperature for 2-4 hours to effect resolution.

The success of the "Metan" method depends upon the tightness of the container, especially of those parts contacting the vapor phase. If the vapor can stream out, the decrease in pressure will cause boiling of the low-water phase and damage circulation of the liquid. This method operates with a saving of heat energy.

Moscicki and Kling³⁵³ proposed a continuous method for separating water present, using a device consisting of an air-tight kettle filled with the petroleum emulsion. The emulsion is heated to 120-140° and held for 2-4 hours at 2-6 atmospheres' pressure, which is usually sufficient for breaking the emulsion. The petroleum emulsion is continuously forced under pressure through a preheating system and then into a vertical receiver, in which the preheated emulsion rises slowly to the top. The dehydrated oil is drawn off by means of a pressure valve and the water is drawn off at the bottom. During the process the kettle content consists of

three phases: water, emulsion, and dehydrated oil, the steam phase being absent in this system. In this respect the process is different from the intermittent method. Weiss⁶²⁸ used a water-insoluble solvent at elevated temperature and a definite steam pressure.

There are only a few instances in the literature concerning the use of pressure alone for dehydration.

Herr²²³ separated water and sludge from petroleum by using compressors. Lacan²⁹¹ produced dehydration of tar by subjecting the liquid to a pressure sufficient to separate the water. Egloff and Benner's¹³⁹ invention applies to the breaking of crude petroleum emulsions by mechanical means, and functions by causing the oil to pass through a series of small orifices under a predetermined pressure. The oil may be treated cold, or heated to any given temperature short of vaporization. The dehydration apparatus comprises a cylinder having a valve-controlled oil inlet, a valve-controlled outlet, and a movable piston adapted to reciprocate within the cylinder. There are numerous restricted passages⁵ throughout the piston. The emulsified oil is forced under pressure. There are means of preventing the return of the oil through the passages when the piston is reciprocated to effect demulsification.

Dyer and Heise¹²⁴ described equipment for demulsification of Santa Maria crude oil, consisting of an apparatus for heating the emulsion and forcing it by pressure through a connected system of capillary tubes (a capillary separator) to break down the globules, and to set free the water contained in the emulsion. Rosenthal⁴⁴² makes the liquid mixture flow with respect to a float valve in a manner that the liquid which is to be retained is pressed aside by the valve.

The application of sufficient pressure to prevent any gas being formed when crude-oil emulsions are dehydrated at high temperatures increases the heating capacity and reduces the water content of the dehydrated oil, particularly with high-temperature electrical dehydration.

Maschinen-Apparaten Fabriken³¹⁴ effects resolution of emulsions by throwing them under pressure upon sharp knives or edges, for example, steel shavings, and then permitting them to settle. In another patent³¹³ resolving of emulsions is performed by heating to temperatures above 100° in a narrow closed receiver having a small gas space. Pressure and temperature are maintained for many hours. The oil layer is withdrawn at once after the temperature drops below 100°.

Parke,³⁷² discussing various plants for the dehydration of gas-tar emulsions, describes pressure and heat dehydration. Brady⁶⁰ patented a combined high-pressure separator and dehydrator for the treatment of petroleum emulsions.

Mineral oils, especially those for electrical insulation, are dehydrated by forcing them under pressure through capillaries, at the end of which they are spread out into thin films over horizontal surfaces. Then they enter a vacuum, wherein the water contained in the oil evaporates.⁵⁸

There are various types of heat treatment in dehydration processes. In choosing among them, it is best to eliminate, if possible, the water

from emulsions by heating them with exhaust steam coils. But in the case of exhaust steam coils the temperature is not high enough, averaging about 170° F. If this method is too slow and inefficient, the next step is to apply direct heating of oil in large boilers.

Boiler heaters are used extensively throughout the oil fields, as this is one of the cheapest and most efficient ways to heat oil. They do not operate under pressure and the temperature is thermostatically controlled. The emulsion may be sent through coils in a furnace heated by hot gases from the burners, preventing direct contact of coils and flames, and recovering the volatile constituents in a condenser. Some emulsified crude oils can be dehydrated at atmospheric pressure with heat applied to the oil, but sometimes it is too slow and tedious and also impractical for certain emulsified crudes. The greatest care must be taken when endeavoring to dehydrate emulsified oils by distillation in a still, since sometimes the emulsion foams or pukes into the receiver and flows over. (Santa Maria emulsified oil, for instance, usually shows such difficulties). In such cases, it is obvious that high pressure or other kinds of treatment have to be applied in addition to heat.

Heat Treatment Combined with Centrifuging and Filtration

Very often heat treatment is used in combination with filtering, centrifuging, electric processes, chemical agents, etc.

Ballard's³⁰ dehydration process for crude petroleum oil involves heating the oil to effect rapid settling of the emulsion as well as of the water in the oil. The water and emulsion are continuously separated from the flowing liquid. The liquid drawn out through the bottom is conducted through a water separator, where the water is removed; the oil and emulsion are then subjected to heat treatment and passed in a thin stream through a second emulsion-separating chamber, provided with inclined plates for recovering the oil therein. The temperature of the dehydrated oil is about 140° F. From the second separating chamber the emulsion not yet destroyed is conducted into a second water separator heated to 200° F, where the water is removed. The emulsion still left is then passed through a centrifugal machine to remove the oil from the water. Loss of low-boiling constituents in the oil is avoided by keeping the oil in closed containers during the heating and separating treatments, and by returning to the dehydrated oil any vapors set free from the oil after collecting and condensing them. The water separator comprises a closed chamber with a series of compartments. The separating compartments have openings in the lower partitions to provide a space between them for a filtering medium containing chat or gravel; special means serve to withdraw water from the separator.

The Apparatus Construction Akt. Ges (Bühning⁶⁹) reports an arrangement for dehydration of fats, oil and hydrocarbons. The oil to be refined is circulated repeatedly by means of pumps from the receiver to a refiner consisting of a filter device and an evaporator. The filter, or the filter and the evaporator, are placed inside of the heating liquid. The

evaporator is surrounded by a hot liquid (above the boiling point of water). The temperature required is decreased by the use of a vacuum, so that the vapors formed in the evaporator are overheated only when leaving it, and condense in a special condenser. The level of the liquid to be refined is maintained by a special device. Usually, even using a special oil evaporator, a large part of the heat is lost by radiation, because vapors coming from the oil are recondensed on the outside walls. This method also prevents mixing of water with oil.

Dahlstrum¹⁰⁰ claims a method in which oil directly heated in a pre-heater is bubbled through hot water against sharp-toothed cones, and is finally passed through electrolytic cells. Copper and zinc strips are used as electrodes. The device used comprises a flow passage having a pair of perforated plates transversely placed.

Little and Sherman³⁰⁵ obtained a patent whose objects were to provide a heating apparatus, in combination with chemical treating equipment, for treating the oil. After it has passed from the heater, it finally enters a separator for eliminating any gas or water remaining in the oil before it is sent to storage. The heating and separating unit includes a boiler-like casing and a fire-box with a casing having a perforated feed tube in its bottom between the flues. A waste pipe extends into the casing.

Kelley's²⁶⁴ process is another example of a combined heat dehydration method. According to it, the oil is heated to a predetermined degree and gradually brought to the desired high temperature by passing it through the ultimate heating step through horizontal passages in a confined column; foaming or ebullition is thus prevented, especially during the time that the oil receives its maximum heat treatment. When the oil is heated, it is directed from the pipe into an electrical treater and subjected to the action of an electrostatic field while being agitated, to break down the emulsion. Pollak's⁴¹² dehydration equipment is a combination of a heat treater and a centrifugal blower. From a perforated partition in a container, oil drips onto a series of horizontal, perforated plates and then flows onto coils of steam pipes. The supply of steam is controlled. Below the drip plates are other coils of steam pipes. The container has a cooling chamber and a conduit provided with means for heating the air. A condenser leads from above the cooling chamber to a centrifugal blower of regulated speed, and another conduit, containing two condensers with receiving chambers, leads from an upper portion of the container to the blower. By automatically varying the area of the heating surface of the steam pipe into which steam is permitted to enter by the thermostat, and by regulating the magnitude of the current of hot air, either by means of the gate or the speed of the blower, the apparatus is adapted for use with varying volumes of oil entering the vaporizing chamber. The condensers are also regulated to adjust the cooling effect to conform to variations in the effect of the vaporizing chamber and to variations in the magnitude of the current from the blower. The flow of oil is effected by

gravity wherever practical, and wherever back-pressure is impossible; otherwise pumps are used.

Weir⁶²⁷ discusses the separation of emulsions by a centrifugal method. An oil which is emulsified in water in minute amounts may be removed from the mixture by adding to it an oil of lower density, stirring the whole to agglomerate the oil particles, and centrifuging to remove the oil.⁴⁶⁷ This centrifugal method has been used principally in the recovery of oil from tank bottoms. The emulsion was heated and then run into a supercentrifuge which separated the oil and water and discharged them separately. These plants were portable and were used chiefly in cleaning very dirty light gravity oils. As far as is known, none of the centrifugal plants has been used for years.

Action of Chemicals and Demulsifying Agents

To dehydrate an emulsion means to remove water from oil. This may be accomplished by producing conditions that influence the stability of the system. Practically all emulsions are formed with the assistance of an emulsifying agent which is adsorbed in the interface as a protective film, decreasing the interfacial tension and imparting stability to the system. From this viewpoint there exists the possibility of dehydrating an emulsion by elimination of the water phase by attacking the emulsifying agent, or by converting it into an ineffective form. The ideal method is to destroy the emulsifier, thus increasing the interfacial tension and permitting coalescence of the disperse phase. To convert the emulsifier into an ineffective form, a substance may be added that either (a) dissolves it and removes it from the interface, (b) flocculates it to such an extent that a coherent film is no longer formed or (c) tends to form the reverse type of emulsion. Chemical methods of dehydrating emulsions are applicable when there is no danger of introducing foreign matter into the mixture, which in itself is already complicated. The components of an emulsion system are always in a certain equilibrium state determined by factors such as electrical charge, solubility, density, viscosity and interfacial tension. A disturbance in these physical conditions may result in a change in the permanence of the system. Experience with commercial dehydration of large amounts of oil indicates that chemical reagents for breaking emulsions do not always act chemically in resolving the emulsion. Some emulsions may be effectively broken by means of agents that do not enter into any combination with the constituents of the emulsion, whereas others require treating agents that are capable of doing so. However, large percentages of chemicals are not necessary for this purpose. The effectiveness of chemicals in breaking emulsions depends, obviously, upon choosing them correctly, upon the nature and properties of the emulsifying agent and, further, upon the manner in which the emulsion is brought into contact with the demulsifying agent. Many of these demulsifying agents are immiscible with the oil, the emulsion, or the brine of the emulsion. Moreover, these oils and emulsions have a high viscosity, so that it is difficult to distribute an immiscible treating agent through them.

Electrolytes play an important part in connection with the stability of colloidal systems, as well as of oil-in-water emulsions. Because of electrolytic dissociation into ions, these electrolytes may prove detrimental or helpful, depending on whether the effective electric charge is like or unlike the charge of the disperse phase of the emulsion. Unlike charged ions result in a discharge of the dispersed particles and act as a factor opposing stability. It is a general rule that coagulation of irreversible colloidal systems occurs by the discharge of ultramicros below the critical potential; therefore, the stability of such systems increases with increase of the potential difference between the continuous and the disperse phase. In regard to the influence of non-electrolytes, cases are known where the stability of colloidal solutions, with respect to the action of electrolytes, increases in the presence of certain non-electrolytes, whereas in other cases it decreases. The reason for this may be seen first in the change of the dielectric constant of the solvent in one or the other direction, and secondly in the change in the adsorption capacity of the dispersed particles. Non-electrolytes which increase the difference between the dielectric constants of the two phases stabilize the system; those decreasing it facilitate coagulation by electrolytes; that is to say, if the adsorption capacity of the disperse phase with respect to the coagulating ions increases in the presence of a given non-electrolyte, the stability of the system drops; if it decreases, its stability increases.

It is a well-known fact that certain colloids are positively or negatively charged, depending upon the character of the disperse phase. Albumin is, for example, positively charged in acid solutions²⁴⁴ and negatively charged in alkaline solutions.⁴⁰⁷ The hydrogen ion is one of the most strongly adsorbed cations, and the hydroxyl ion one of the most strongly adsorbed anions. Strongly adsorbed cations neutralize the negative charge on the particles and precipitate the water. The ferric ion is adsorbed to such an extent that it will carry the particles over from a negative charge through the isoelectric point to a positive charge, in a manner analogous to the reversal of the charge on albumin particles.

On the other hand, the dehydrating action of certain commercially used demulsifying compounds is probably due to the fact that they are hydrophilic colloids. Just as there is a selective adsorption of ions, so there is a selective adsorption of colloids. As the precipitation of colloidal particles is due to the adsorption of an ion having a charge opposite to that on the particles, so colloids of opposite character precipitate each other. Hydrophilic colloids should actually discharge an emulsion formed by the use of a hydrophobic colloid, and a hydrophobic colloid should discharge an emulsion formed by the use of a hydrophilic colloid. But in the destruction of an emulsion formed by a hydrophobic colloid, it is not necessary that the hydrophilic colloid should have an opposite charge. Thus, for example, we have negatively charged soap micelles⁴⁷⁰ in water caused by adsorbed hydroxyl ions precipitating the negatively charged water particles of these emulsions.

Hydrophilic colloids soluble in water are strongly interfacial. Modern

emulsion-treating practice makes little use of aqueous solutions of treating chemicals and, where it does, the chemicals are dispersible in both water and oil. The great difficulty of breaking water-in-oil emulsions by adding chemicals in aqueous solutions lies in conveying the latter through the enveloping oil to the dispersed water, which they must reach to be effective. It is possible to convey the positive ions through the enveloping oil when a substance soluble in both water and oil is used. Experiments showed that a small percentage of acetic acid (acids ionizing readily are very effective), in the presence of such a substance is more effective in breaking emulsions. The substance soluble in both oil and water conveys the acid through the enveloping oil to the dispersed water and when that comes in contact with water the hydrogen ion of the acid neutralizes the negative charges thereon and establishes conditions favorable for coalescence. Any substance capable to dissolve in oil and water should be expected to act in this manner. Phenol is the most satisfactory; kerosene and acid sludge contain such substances but have to be used in large quantities to be effective. When a small amount of phenol is added to kerosene-acid sludge, the mixture is more effective for breaking emulsions than the phenol and acid. The amount of acid necessary is very small. According to Dodd,¹¹⁵ a substance soluble in both phases of the emulsion may serve in the resolution of crude petroleum emulsions. The effect of oil-soluble substances can not be predicted by their solubility in water alone; other properties are also of importance. In the case of petroleum emulsions, the emulsifier (in many cases asphalt) and the presence of a strongly adsorbed positive ion have to be considered.

The effect of two-phase solubility has been proved sound only for some cases, because highly effective treating agents are found among those that are completely insoluble and non-dispersible in water. Electrolytes with strongly adsorbed positive ions can be substituted for the acids provided they are soluble in the two-phase soluble substance and can be led through the oil to the dispersed water. Ordinarily, this is rather difficult when electrolytes alone are used and even then only when they are present in excessive amounts. It is known that the coherence of the film of the emulsifier depends upon the nature of the oil; an excess of light fractions seems to promote the formation of the protective film. The dispersed water globules of the majority of petroleum emulsions carry negative charges decreasing the surface tension in the interface (however, many Oklahoma emulsions are positively charged). It was believed that when these charges are neutralized, surface tension increases to such an extent that the films are not able to prevent coalescence, and the emulsion breaks.* Past experiments have shown that many emulsions are chemically resolved without appreciable alteration of the interfacial tension. Auerbach¹⁴ proved mathematically that the effect of electrostatic expansion tension of the charge in decreasing interfacial tension is negligible. The resolution of these emulsions becomes obvious

* *Chem. Met. Eng.*, Feb. 7, 1923.

even by a change in their appearance. Some petroleum emulsions are chocolate brown in color. When the water globules coalesce to macroscopic sizes, the color changes to black. This change in color seems to be quite an accurate indication of a change in the degree of dispersion of the water. The stability of petroleum emulsions is attributed to the presence of various high molecular weight hydrocarbons, such as petroleum resins, asphalts and asphaltenes. On the other hand, salts included in the water act upon the free organic acids of petroleum to form alkaline-earth soaps, principally calcium soaps.²⁰⁷ Dehydration is possible if the action of the colloids already present is neutralized. The most important factor in securing agglomeration is to destroy the effect of the protective colloid. The reaction may not destroy the colloid itself, but it may be sufficient to throw it out of the aqueous solution, either by precipitation or extraction,²² the latter being carried out by rendering the colloidal substance soluble in the oil phase of the oil-in-water emulsion. On the other hand, the agglomeration effect may be based on the tendency of weak acids to decompose the alkaline protective colloids without splitting the soap, although not every impurity in the oil phase of a soap-water emulsion acts as a protective colloid. Boric acid is an example.

The acid impurities dissolve in the oil, thus reducing greatly the permanence of the oil-in-water emulsion system. Any treatment based on the elimination of the protective colloid is likely to be limited in its efficiency to a fixed concentration of the pure oil with a pure soap solution. A condition that reduces the degree of dissociation of soap in the solution still further increases the yield of the oil. Commercial soap-water emulsions commonly tend to gelatinize. Pure soap solutions gel when the soap concentration is high enough, but the gel is in a rather unstable state—either a small addition of water or a slight increase in temperature destroys it. Gels formed by many commercial soap-water emulsions are of a more persistent stability. The emulsion retains its gelatinous character even after considerable dilution with water or on using higher temperatures. Some emulsions in a gelatinous state contain from 56 to 60 per cent of water. It may be inferred that they resulted from a partial precipitation due to an insufficient positive ion adsorption. If this is the case then, according to Sherrick, hydrogen ions should cause the discharge of these gels. Therefore, he treated stiff gels with varying concentrations of hydrogen ions, but in no case were the gels once formed destroyed. This led Sherrick to assume that particles composing the gel were no longer charged negatively and that the stability of these gels was influenced by the proportion of protective colloids present. In the case of non-fatty acids in aqueous alkaline solutions, persistent semi-gels are formed; they are not as rigid as pure soap gels, but they are more stable. The impure industrial emulsions, when gelatinized, are probably of the same persistency and semi-gelatinous consistency. The viscosity of the semi-gels is gradually reduced with rising temperature. Even boiling does not always destroy the gelatinous characteristics. The agglomeration state of a semi-gel may be destroyed so that it liquifies only by

dilution with water, or by chemical action. When sufficient water is present, the viscosity of the emulsion is not greatly influenced by a change in temperature.

Chemical treatment of gelatinous emulsions shows that conversion into a liquid state takes place almost without any physical change (heating, cooling, agitation, dilution). The addition of a trace of mineral acid to a gelatinous emulsion often causes liquefaction. A little agitation may restore the gel. Another trace of acid may again liquefy it, and another agitation may cause a reversion. This cycle of reversibility is repeated until the soap is completely decomposed.

Chemical treatment of oil emulsions often involves the use of water-softening agents. Different oil emulsions require treatment with varying chemical mixtures. Emulsions are sometimes called "tight" or "loose."³⁸³ These terms refer to the stability of the emulsion when subjected to various tests. Emulsions may be "tight" because of their extremely small particle size. But on the other hand many gas-tar emulsions, for example, contain macroscopic water particles and yet are extremely "tight." The tight emulsions are hard to coalesce or to break, and do not separate into oil and water even over a long period of time. Loose emulsions are often broken merely by heating the oil, and settle out on standing. Experimenting with an emulsion from a Texas field, Sherrick⁴⁷¹ found that the water globules carry a negative charge, and that the water can be precipitated by neutralizing this charge. The efficiency of acids in neutralizing the charge was found to be directly proportional to their hydrogen ion concentration. Efficiency of acids followed the order hydrochloric, sulfuric and acetic. Other electrolytes with strongly adsorbed positive ions also neutralized the charge and precipitated the water. Furthermore, Sherrick stated that the extent to which the negative ion is adsorbed with the positive ion is of considerable importance. Dodd¹¹⁵ claimed that the order of efficiency of acids is the reverse of that found by Sherrick, and pointed out that in all cases of chemical treatment considerable heat and time are necessary factors.

Kuczynski²⁸⁷ stated that, if a crude-oil emulsion does not separate when heated under very high pressure according to Mosciicki's method, it must be blended with one or several emulsions having large-sized particles; under ordinary conditions perfect and quick separation is thus provided. Mixing of two or more suspensions differing in particle size makes it possible for the suspensions to settle out more readily. He also recommended the addition of phenols, cresols, xylenols, and poly-phenols. As mentioned above, these additions increase mutual solubility, which is one of the principal factors in the chemical treatment of emulsions. Benzene and petroleum produce less stable emulsions, says Kuczynski, than lubricating oils, the solubility of which in water is very slight, usually decreasing with decrease in specific gravity. By the addition of benzene, benzene, alcohol, ether, and a simultaneous increase in temperature, solubility is increased, and this assists in breaking down the emulsion.

Emulsions from the Panhandle (Texas) contain a very concentrated

brine, while the oil contains notable quantities of hydrogen sulfide. Since crude oil is less soluble in a salt solution, emulsions containing natural salts are sweetened.³⁸¹ Gurwitsch²⁰⁷ explained this process by a decrease in the surface tension produced by the action of the recommended additions, which take the place of the emulsifier when the latter is removed from the oil/water boundary. Added benzine, benzene and alcohol, according to W. Ostwald,³⁶⁸ may be shaken out with a third substance; the solubility of the oil in this third substance, and not in the water, plays the significant part. It is known that a definite mixture of benzine, alcohol, and ether has the property of precipitating asphalt from petroleum at certain concentrations. Lottermoser and Calanter³¹⁰ considered a similar phenomenon for the destruction of emulsions.

Ayres²⁵ pointed out that sour oils are usually neutralized with caustic soda, the reaction products being soap and sodium sulfate, and also some free alkali. A water-in-oil emulsion is formed; this type being due to adsorption of the basic radicals of the inorganic salts and the alkali present. That the resulting soap in such emulsions is distributed in the continuous oil phase is indicated by the fact that the mere contact of additional water in these emulsions causes their breakdown. The addition of water extracts soap from the oil. It is standard practice to percolate water through alkaline emulsions or to agitate the emulsions with certain amounts of fresh water. Acid-treated oils from which all traces of excess sulfuric acid have been removed by washing with water and filtering through adsorbents, such as fuller's earth, can be agitated with caustic soda solutions to remove the dissolved organic acids without the formation of stable emulsions, because no sodium sulfate is present to precipitate the soap. The absence of sodium sulfate seems to account for the lack of emulsification. On the other hand, as petroleum soaps are very soluble in water, they function as hydrophilic emulsifiers only in the presence of a sufficient percentage of an electrolyte. Hydrophilic colloids cannot aid in the separation of alkaline emulsions. For the resolution of alkaline emulsions the presence of sufficient water to extract the soap from the continuous oil phase is necessary. About 20 to 60 per cent of water is usually added to the alkaline emulsion and the liquids agitated for better contact. The hot mixture is then centrifuged, using comparatively high throughputs. Graaff¹⁸⁵ heats the crude with fresh water in a container which is connected with a cooler, until drops of water are formed in it. The oil is then permitted to settle, and after the water has been drawn off it is distilled.

In some treating plants, the demulsifying chemical is introduced into the oil through the same type of feeder as is used on flow lines. The treating plant³⁶⁷ functions by putting the emulsion through a series of baffles under pressure. The baffles in the line are merely 3-inch gate valves, whose gates are perforated by seven or eight $\frac{3}{8}$ -inch holes. By using gate valves the unnecessary baffles can be cut out by opening the gate. A screening tank removes the dirt accumulated in the emulsion. The oil in the screening tank is reheated by means of a water heater

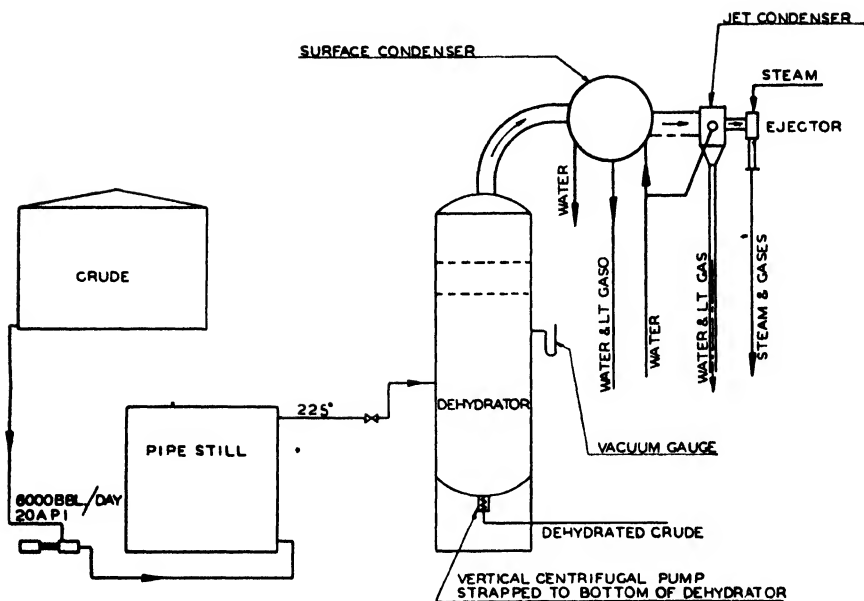


FIG. 14. Diagrammatic Sketch of Vacuum Unit at Lion Oil and Refining Company's Plant at El Dorado, Arkansas.

made from pieces of discarded outside tank casing. Passing the oil through baffles under pressure permits the treating chemical to function more efficiently. (The Oil Reclaiming Company claims a high speed of emulsion resolution—more than a hundred barrels an hour.)

Webb,⁶²⁵ in an article "Field Methods of Treating Oil in North Texas-South Oklahoma," states that the treating method for "BS" practically the year round, and especially in the colder weather, involves the use of both chemicals and heat. The chemical is added to each stock tank bottom. The bottom plus chemical is then stirred up and allowed to settle, after which the tank is filled with fresh crude. The entire tank of oil is then circulated through a gas-fired heater until thoroughly warm from top to bottom. This gives the chemical a good chance to mix with the warm oil and finishes the process of treating.

S. Dayson^{103a} (Lion Oil Refining Co., El Dorado, Arkansas) developed a method of breaking down emulsions and separating water by the joint application of heat and vacuum and simultaneous use of chemicals. The vacuum ejector is designed to secure a vacuum from 75 to 150 mm (absolute pressure), depending on the nature of the crude charged. The reduction of vapor pressure due to vacuum is such that the pipe still outlet temperature is reduced to 220-230° F. At this temperature no trouble is experienced from salt deposition in the tubes. The whole system is under almost complete automatic control.

In addition to selecting the proper chemical to be used, it is equally important that it be applied at the correct point in the system. This

may involve down-hole treating, which has been found successful, or introduction of the chemical by various types of pumps or lubricators at the proper time and place on the surface.²⁹⁸ Sometimes the lubricator is connected close to the well head in order to obtain maximum agitation and also to act upon the emulsion before a too complete stabilization takes place.

Treating chemicals are applied to the emulsified crude in several different ways. The two common methods are known as "lead-line" and "down-the-hole" treatments. In the case of lead-line treatment the chemical is injected into the lead line somewhere between the well and the heater. In down-the-hole treating the chemical is either poured or pumped down the annular space between the tubing and the casing with either water or fluid from the well put down behind it to wash it thoroughly to bottom. The chemicals may be pumped by means of small chemical proportioning pumps varying in size, capacity and operation. There are ratchet-driven and belt-driven pumps, as well as electrically-driven pumps. The pumping capacities range from 1 pint per 24 hours

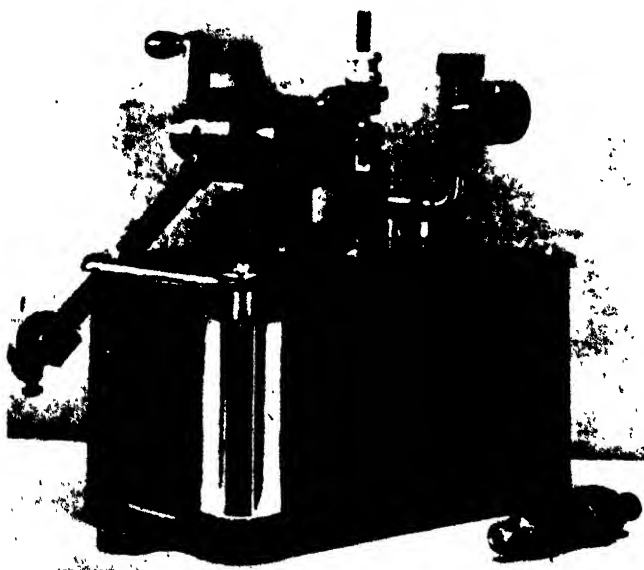


FIG. 15. One of Several Types of Chemical Proportioning Pumps Used in the Seminole Area.

to 2 and 3 gallons per 24 hours, depending upon the size of the plunger, and the length and number of strokes. Most pumps have reservoirs with capacities ranging from 4 pints to 3 gallons.²⁵²

Pumps suitable for treating petroleum oils with emulsion-breaking reagents are described by Henry and Sullivan²²⁶ (Figs. 15 and 16).

Down-hole treatment involves pumping the chemical into the casing-head, a small stream of the fluid from the lead line being allowed to go into the casinghead with the chemical to wash it to the bottom of the hole. The lead line is tapped at some convenient point close to the well head above the casinghead so that a sight-feed can be installed; and the



FIG. 16.

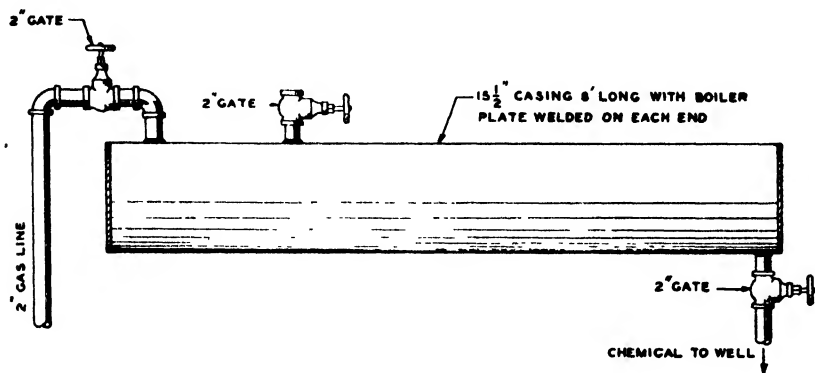
Chemical Feeding
Pump Driven by $\frac{1}{4}$ -
Horsepower Motor.

fluid going down the casing with the chemical is adjusted to suit the operator's idea of the correct amount. When chemicals are used, the best practice is to get them into the oil as soon as possible. It is better at the well than at the plant, and at the bottom of the hole it is believed to be the best of all.⁴⁴³ The chemical should be added in a fine stream, preferably through a perforated screen, so that chemicals which are heavier than the oil will not settle to the bottom before mixing with the oil. Usually there is sufficient agitation of the emulsion with the chemical to "break" the emulsion by the time the fluids reach the treating system. The flow of the production through the well or surface lines agitates the emulsion. However, in certain areas [Panhandle (Texas) and Jal (New Mexico)], the emulsion requires additional agitation. In these areas the first tank in the treating system is used in the capacity of an agitating tank. The fluid from the well enters the agitating tank through a spreader 3 to 5 feet from the bottom of the tank. There is no gas separator or "boot" between the well and the spreader in the agitating tank. The oil-water contact level is controlled by an automatic water control below the spreader. The gas coming through the lead line with the crude oil and water agitates the tank continuously. Additional agitation may be effected by means of a gas spray connected to the lease gas supply. The spray is placed in the tank at the same level as the spreader. The oil leaves this tank approximately 4 feet from the top and gravitates either to a settling tank or to the stock tanks.⁴²³

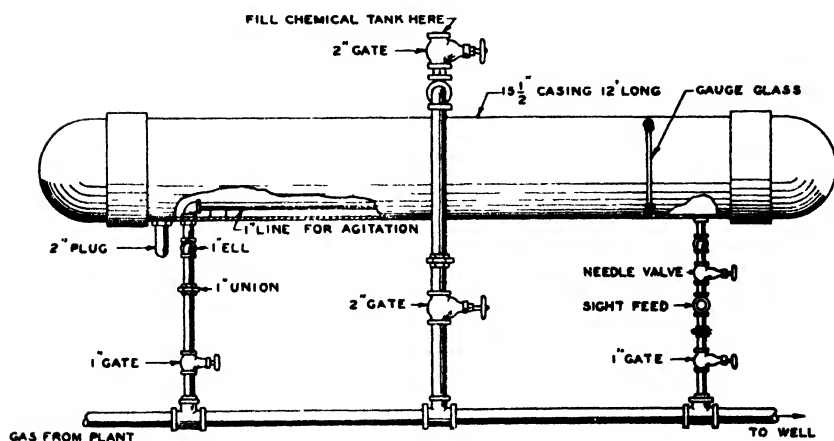
It is the custom to place the lubricator on the wells cutting most, as these make the most gas and have the most agitation. Some companies use a header system and lubricate the chemical into the oil at the header before passing it through a series of baffles to the heating plant. The header system has the disadvantage of putting an unnecessary pressure upon the lines, which may have a detrimental effect upon the equipment

and production. The distribution of chemicals is carried out either by a low-pressure down-hole chemical lubricator, or by a typical high-pressure down-the-hole lubricator as shown in the attached sketch (Fig. 18). Treating down-the-hole not only reduces the chemical cost, but usually eliminates the use of heat on the surface.³⁴⁷

Bignell,⁵² describing the test of a drill in Oklahoma, mentions the inverted type of lubricator for the injection of the chemical into the lead lines or down-the-hole (Fig. 19). The chemical has a greater carrying effect and contacts more of the oil if diluted with water. Care must be taken in the selection of the water, because the chemicals used are pri-



LOW PRESSURE DOWN HOLE CHEMICAL LUBRICATOR
FOR
BATCH LOTS



HIGH PRESSURE CHEMICAL LUBRICATOR FOR USE WITH DOWN THE HOLE METHOD

FIG. 18.

marily water-softeners and much of their strength should not be used in softening excessively hard water. The chemical must be applied in the form of a fresh soft-water solution. The strength of the latter may be from 5-25 per cent. A typical treating plant consists of one or more lubricators, either force- or line-pressure feed, placed at the most advantageous position. The advantages of down-the-hole treatment are: (1) no heat is required to get a good treatment; (2) less chemicals required than when oil is treated on top of the ground. Instead of constantly feeding a small amount of solution, a given amount of chemical solution may be injected into the well once or twice each day. It is not necessary to inject the chemical solution into all wells—only a part of the wells

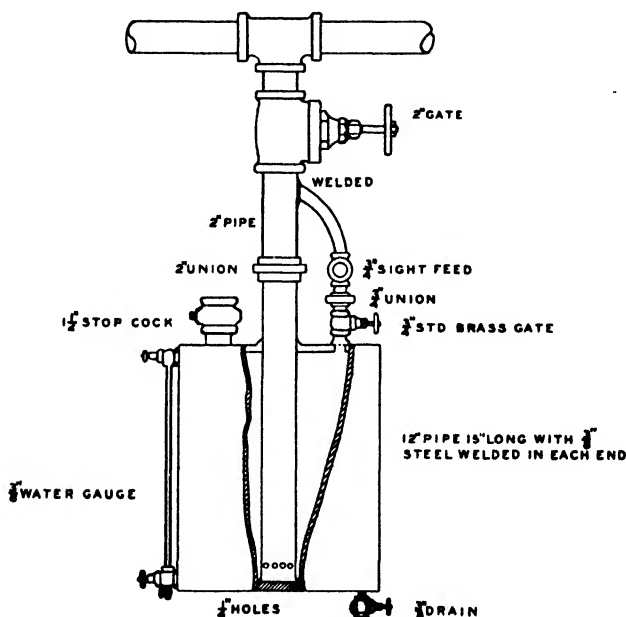


FIG. 19. Inverted Lubricator.

that are pumping into the same settling tank or gun barrel are usually treated. These are the wells with the highest percentage of emulsion or basic sediment (determined by centrifuging tests) and the highest production. When wells are under vacuum, the chemical solution is applied through a copper tube extending into the well casing a few feet below the vacuum line, the vacuum on the well pulling the solution into it. The solution is prevented from passing out through the vacuum line by closing the valve on the vacuum line while the chemical is applied. In the case of wells open to the atmosphere, all that is required is a bucket or a can, and the chemical solution is poured into the well through the casinghead. The amount of chemical used is based on the amount of net oil the well produces.¹⁶¹

Re-emulsification may take place even after a chemical is added, and conditions causing it must be either removed or corrected; otherwise the emulsions in the wells are not susceptible to down-the-hole treatment. If the chemical is added to the cut oil in a flow line (between the casing-head and the gas trap), or to a gravity flow line leading from storage tanks to the treating plant, then a container known as a chemical lubricator is often installed on the line. Fig. 20 shows (a) the air vent which is opened; (b) the funnel through which the chemical is poured until the

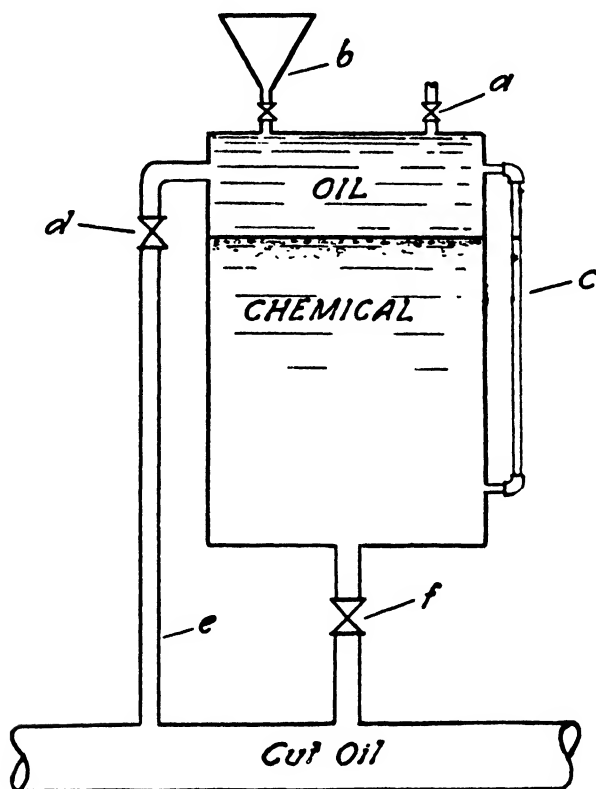


FIG. 20. Chemical Feeder.

gauge glass (c) shows that the lubricator is full; (d) is a valve on the by-pass line (e) to be opened for admitting gas pressure above the chemical; (f) is the discharge valve, regulated to obtain the best mixture in the flow line. This type of chemical feeder requires little attention after once being regulated.

Fig. 21 illustrates a combined chemical and heat-treating method at a flowing well or at a well operated by air-gas lift. In the sketch shown (a) is the chemical lubricator installed on the flow line; (b) the oil and gas separator; (c) the oil discharge line; (f) the preheater heated by

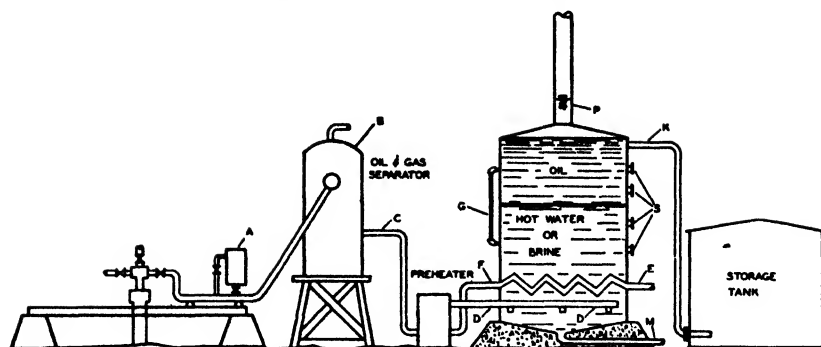


FIG. 21. Combined Chemical and Heat-treating Method.

exhaust steam; (e) the place where steam enters the treater and circulates through the steam coils heating the brine and the oil; (g) the gauge glass indicating that the treater is kept full of salt water up to about $\frac{1}{2}$ or $\frac{2}{3}$; (s) the stop-cocks by which the fluid column may be checked at intervals; (p) the pressure relief valve serving to protect against failures due to excessive pressures; (m) the drain line connected to the center of the tank bottom for removing at intervals sand, silt, and some "BS," and (k) a line that skims off clean oil which gravitates to storage.⁸⁸

The National Oil-Rator, installed by the Berry-Asphalt Co. of Waterloo, Arkansas, and described by Smith,⁴⁸² is an emulsion-treating plant using a combination of heat and chemicals. The installation works as follows: raw oil is taken from storage (1) by a steam pump (2) which is operated by flow control A. The chemical is added at C and the oil

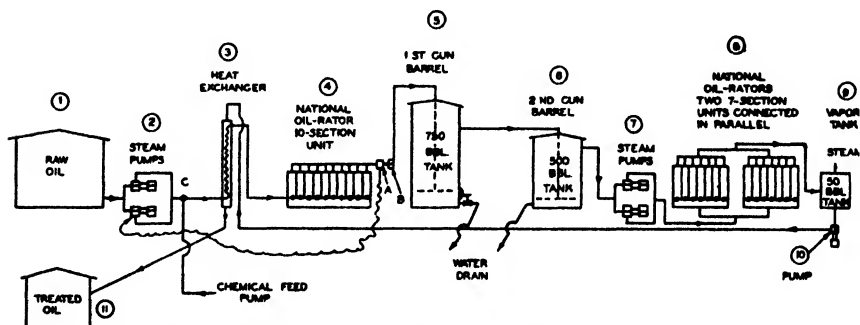


FIG. 22. Flow Diagram of National Oil-Rator Treating Plant.

passes through a heat exchanger (3) at a temperature of 210-220° F in the 10-section Oil-Rator unit (4). Thereby 60 per cent or more of the water separates out in the gun barrels (5) and (6) and is removed from the system. The oil is then moved by a steam pump (7) through two parallel connected 7-section Oil-Rators comprising the heater unit (8), where it is heated to 240° F. The remaining water flashes off as steam

in the water-vapor tank or evaporator (9). The treated oil is pumped from this tank by a pump (10) through the heat exchanger (3) and then to the storage tank (11) (Fig. 22).

Roberts⁴³⁴ states that in the chemical resolution of petroleum emulsions not only are the point of introduction of the chemical, the kind, amount and strength of the chemical solution, and the temperature of treatment important in determining the efficiency of the treatment, but also the degree and duration of agitation of the system. Although agitation is the dynamic factor in producing an emulsion, it is just as important in destroying it. In the latter case, it must be neither too severe nor too prolonged. The purpose of agitation is to accelerate penetration of the chemical throughout the oil to the interface. The agitation must suffice to cause impacts that lead to coalescence of very small droplets, but, if too vigorous, it will cause still smaller droplets to form. The

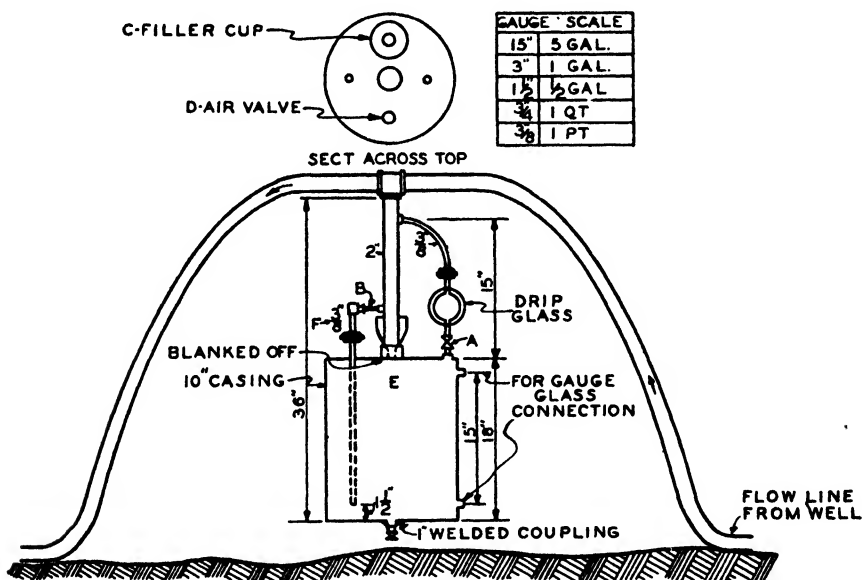


FIG. 23. Sight Feed Automatic Chemical Lubricator.

duration of agitation must be such as to provide time for the chemical to reach the interfaces and produce droplets of a size sufficiently large to coalesce in the settling tank.

The typical treating plant operates continuously. The fluid mixture is introduced into the tank near the bottom on one side, while separated water is drawn from the bottom on the other side and pipe-line oil flows from the top into the stock tanks. The fluid is fed continuously into the tank, called a "gun barrel." An upward flow of oil is effected in the tank, against which the coalesced water drops must settle in order to separate. It is very important that the size of the tank and especially its diameter

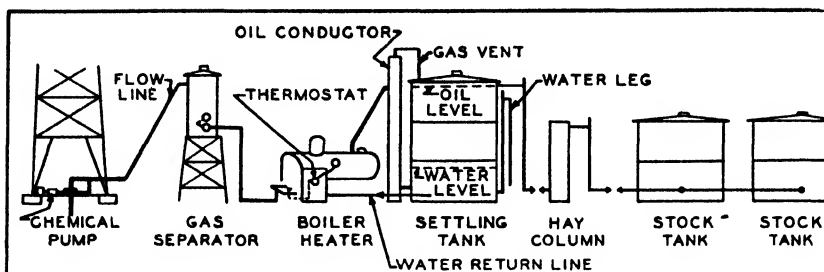


FIG. 24a. Typical Chemical Treating Plant.

be suitably chosen with respect to the volume of production, so that the vertical velocity is not excessive. There is a limiting velocity above which effective settling does not take place. This velocity is determined by the size of water drops, gravity differential, and viscosity of the oil.

Two types of lubricators are used for feeding chemicals into flow and lead lines for treatment of cut oil in the oil fields: (1) the positive or force-feed type, and (2) the automatic sight-feed type. In the first, the chemical is forced into the line by a small plunger pump driven by a motor. This type is most efficient, but power to drive the pump is not always available. In the automatic type the method of feeding depends on gravity displacement. The purpose of a lubricator is to establish against the existing line pressure a continual and uniform feed into the line, so that a minimum quantity of the chemical effectively treats the cut oil. The dimensional sketch of an automatic sight-feed chemical lubricator used in the Seminole area by the Tidal Oil Company is shown in Fig. 23.

The lubricator is filled with the chemical through the cup, *C*, with valves *A* and *B* closed and air valve, *D*, open. Then air valve, *D*, is closed and valve *B* opened. The feed is regulated to the desired amount

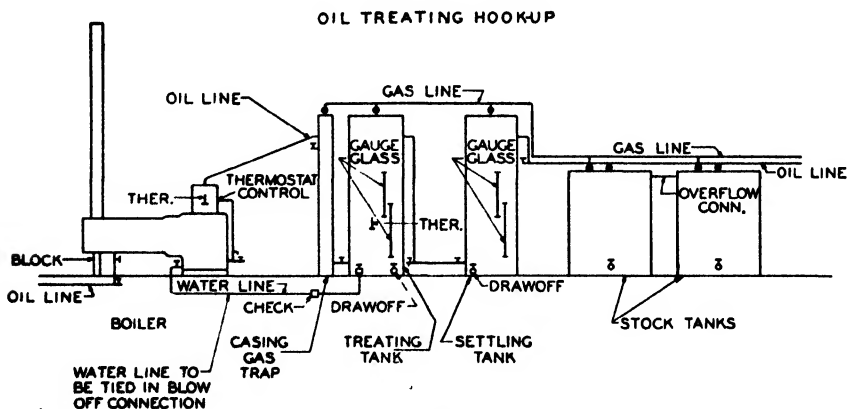


FIG. 24b.

by valve A. The quantity and rate of feed of chemical into the line are based on tests made at varying intervals, depending on the type of the well and the character of the emulsion.

Fortine,¹⁶² in his article on "Oil Treating Methods," illustrates diagrammatically a typical chemical treating plant as shown in Figs. 24a and 24b.

In any treating project, there is a certain combination of heat and chemical by which the best results are obtained. In the case where cut oil comes from one or two wells, lubricators are placed near the well. If several wells are cutting, they are run into a header with a chemical lubricator attached through a series of baffles into the receiving tank. This method is used when no heat is available and the amount of emulsion is not too great. When a separator is used, the chemicals are introduced before the oil reaches the separator. On gas-lift wells, the chem-

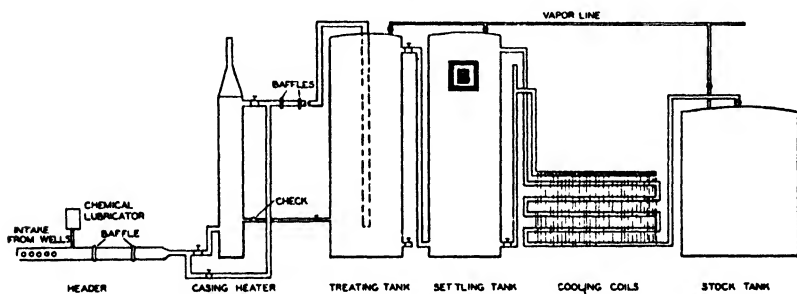


FIG. 25. Typical Heating Plant Installation for Treating Cut Oil Used by the Barnsdall Oil Co. in the Mid-Continent.

icals are often lubricated into the gas input lines. The sketch in Fig. 25 shows a typical heating plant installation. The oil, after leaving the second settling tank, is subjected to cooling by cooling coils for reducing the temperature of the oil before it is run to the stock tank. Heat exchangers aid in reducing the amount of steam.

Demulsifiers

Van der Minne^{612a} has suggested that demulsification is based on the fact that a demulsifier of a contrary type is introduced which destroys the power of the emulsifier present in the oil. The demulsifier destroys or diminishes the protective action of the emulsifier in the interface. Different chemicals react in numerous ways. One group tends to take up the water and form another substance. Another group reacts with the salts in the water. Another group tends to dissolve the material making up the protective film. And still another group tends to rupture the protective film.

Chemicals act directly on the film around the globule of water, tending to rupture, dissolve, coagulate, or soften it to the extent that, by gravity and its own weight, the water ruptures the film surrounding it,

coalesces, and drops out. The chemicals proposed for breaking emulsions are roughly divided into:

(1) Agents such as calcium chloride and quicklime.

(2) Agents which flocculate substances composing the protective films, such as sodium chloride, ferric chloride, sodium sulfate (not very effective).

(3) Agents presumably reacting with organic acids or their salts present in the external phase of the film, such as caustic soda, lime, and sodium bicarbonate. For example, when these react with naphthenic or similar acids they form water-soluble soaps reversing the water-in-oil emulsion and breaking it.

(4) Agents that break the protective films by reversing the type of emulsion and acting as stabilizers for the oil-in-water type. Such are the iron oxides and other finely divided salts, clays, silica, soaps, gums, starches, albuminous matter, etc.

(5) Agents such as electrolytes which presumably neutralize the electrical charge of the dispersed water droplets, such as sulfuric acid, acetic acid, salt solutions: ferric nitrate and ferric chloride.

(6) Agents that are solvents for the material making up the protective film. Carbon disulfide, carbon tetrachloride, benzene, acetone, alcohol, ether, and gasoline. These substances also decrease the viscosity of the external phase and thus reduce the stability of the emulsion.

(7) Commercial demulsifiers.

In selecting demulsifiers there is no manual for determining in advance which of them is most suitable. The idea that the determining factor is whether the oil has a paraffin or an asphaltic base does not hold true in many cases. If it were true, paraffin-base oils should preferably be treated with sulfonated fatty acid compounds, and asphaltic base oils with petroleum sulfonates. The modern demulsifying agents for water-in-oil emulsions are substances which are highly adsorbable either as such or in the form of alkaline-earth salts. The emulsifying agent must be polar in order to adsorb on the oil side of oil/water interfaces. The ordinary commercial demulsifying agents or their alkaline-earth salts, which are adsorbed on the emulsifying agent, are invariably polar. Polar compounds are characterized by having an electric dipole, *i.e.*, the electric center of gravity of the negative charge of the electrons does not coincide with that of the positive nucleus. Polar molecules have a finite average dipole moment. All inorganic acids, bases and salts belong to the group of polar compounds in which atoms are supposed to be held in electrostatic union. Non-electrolytes or organic compounds, the atoms of which are supposed to be held in electromagnetic union by sharing a common pair of electrons, constitute the group of non-polar compounds. Polar substances are adsorbed more readily than non-polar, and when the former are adsorbed they saturate the residual outside valences and are more effective per unit of mass. Residual unsaturated valences exist to an optimum extent at the interface of two phases and attract the added demulsifying agent to this interface. Frequently polarity of chemical

compounds is meant in the sense of introducing an ordinary hydrophilic group or atom into a hydrophobic body or residue, for example, the introduction of the sulfonic group (SO_3H) into a benzene residue.

Melvin de Groote^{180a} (Tretolite Co.), to whom we owe the greatest number of demulsifying agents, considers demulsification as an offset of secondary valences or nuclei of polarity. For the action of the principal groups of demulsifiers (1) oleyl-hydroxystearic acid or an ammonium salt; (2) oleic acid hydrogen sulfate: mono-, di-ammonium salts; oleo-sulfonic acid: ammonium salt; (3) benzene sulfo-stearic acid: ammonium salt; (4) petroleum sulfonic acids and their ammonium salts, de Groote distinguishes five features of significance:

(1) They give colloidal dispersion in oil and tend to be adsorbed at the oil/water interface.

(2) They contain hydrophilic and hydrophobic groups oriented at the interface between oil and water.

(3) A radical, which combines with a calcium or magnesium atom, forming an insoluble salt, is present.

(4) Another group, radical or residue, is introduced into a hydrophobic group or radical.

(5) Two nuclei of polarity are present in oleic acid or sodium oleate. In modified fatty acids or their salts or esters there are three nuclei of polarity (exemplified by secondary valences).

Definite requirements were postulated for emulsion-breaking compounds, namely, (1) the antagonistic effect (good emulsifier for the reverse type of emulsion); (2) solubility in water and preferably more or less in the oil. Van Dedem¹⁰⁵ considered three other factors to be significant. The compound serving as demulsifier should preferably be wetted by water in order to obtain maximum adsorption in the water phase at the water/oil interface. The compound added in small percentage should not react chemically with the salts dissolved in water, nor should it change materially the pH of the salt water. For soaps which are completely insoluble in oil, a small degree of hydrolysis is required to make it possible for the fatty acid radical to reach the water globules through the oil phase. Finally, compounds should not introduce difficulties during subsequent handling and refining of the crude oil. Compounds causing persistent discoloration of gasoline have a tendency to form emulsions during the refining process or give the oil an acid reaction which causes corrosion, and their use should be avoided.

The requirement that the pH of the salt water should not be changed by the chemical, according to van Dedem,¹⁰⁵ follows from the fact that most soap solutions show optimum demulsification when they are partially acidified with a strong inorganic acid, before insoluble acid soaps or fatty acids start to precipitate. The salt water in the emulsion very often is buffered by alkaline salts of weak acids, such as carbonic acid or weak organic acids. Such a soap must be selected so that the pH of the salt water corresponds to, or is slightly lower than, the optimum value required for demulsification of the soap. If the pH of the water is much

lower than the optimum value, the soap will be hydrolyzed too much; if the pH is higher, the alkaline-earth soap precipitates.

Van Dedem's experiments showed that partial hydrolysis of Turkey-red oil or of castor oil soap is essential for complete separation of the emulsion, and that sulfonated products having a greater stability against acids and alkaline earths, due to a decreased hydrolysis of the sulfonate group, always give a smaller effect. However, it is well known that sulfonated products are much more effective agents than castor-oil soap or Turkey-red oil.

Van Dedem,¹⁰⁵ studying the chemical methods for separating petroleum emulsions, came to the following conclusions: (1) analysis of edge water of every separate drilling project in an oil field must give the proportion of carbonate, bicarbonate, weak organic acids, sulfate, the total hardness, and the pH value; (2) titration curves and the pH value for optimum demulsification of the dehydration compounds must be considered. The optimum demulsification must correspond to the pH of the salt water; (3) in the case of alkaline water of high pH, containing likewise little alkaline-earth salts, neutral soaps of oleic acid, solid fatty acids, liquid saturated fatty acids, linoleic acid, etc., should be applied as demulsifiers; (4) in the case of alkaline water of lower pH buffered with bicarbonate, neutral or weakly acid ricinoleate, other oxy- acids or resin soaps should be used. Instead of ricinoleate, Turkey-red oil, with the sulfonate group esterified and loosely linked, may be used for more economical results; and (5) in the case of acid water, soaps of naphthenic acids having a low sulfate content, and the more stable fatty acid, aromatic sulfonates, having a higher sulfate content, should be applied, provided these are adapted to the pH of the water, and have no antagonistic constituents.

Factors determining the effectiveness of any treating compound in resolving an emulsion Roberts⁴³⁴ calls "characteristic" of the emulsion and summarizes them briefly as (1) the kind of emulsion, (2) the kind of chemical, (3) how they are put together and (4) what happens afterward.

The necessity for correlation between conditions in the emulsion and the type of demulsifier used is strongly emphasized. Two requirements are postulated for the chemical used: (1) its concentration must be such that it is miscible with the system, nullifying the effectiveness of the stabilizing agent; (2) it must be able to act upon the substances at the interface as the time treatment is applied (this time factor is a function of the age of the emulsion).

The efficiency of treatment with a chemical depends on: (1) the point of introduction of the chemical, (2) the degree and duration of agitation of the system, (3) the kind, amount, and strength of chemical solution, (4) temperature of treatment.

Monson³⁴⁸ pointed out that the choice of a reagent for the resolution of an emulsion depends upon the temperature at which the selection tests are conducted. It was observed that an emulsion which required one

reagent when the oil was treated at 110° F was not suitable for one treated at 80° F. Monson stresses also the importance of greater ratios of recovery. The recovery of clean oil or dry oil to one part of reagent has enormously increased since the early days; whereas producers then were fortunate to recover 1000 parts of oil with one part of reagent, today the usual ratios of reagent to recovered oil are from 1:5000 to 1:30,000, or 1:40,000.

According to Shea,^{468a} the success of treating "cut" oil chemically depends upon: (1) an adequate quantity of a suitable chemical; (2) sufficient agitation to cause thorough mixing of the chemical with the emulsion; (3) addition of heat to facilitate resolution; (4) proper handling and separation of gas before settling; and (5) standing for a long period of time to permit settling out of water.

Shea ^{468a} observed that the introduction of a small quantity of chemical into the lead line upstream from the surface choke or flow bean prevents or lessens emulsification in the bean. In some gas-lift wells, equally effective results are obtained by injecting chemicals immediately ahead of the flow bean instead of down the hole. According to Roberts ⁴³⁴ different compounds are required depending upon whether treating is done in the well, in the flow-line, in lease tanks, or tank bottoms.

Sometimes compounds are even changed at appropriate intervals during the productive life of a well. The changes in the character of the emulsion are rather slow and occur over long periods; thus few changes in the compound are necessary during the life of a well.

The point of introduction is important with respect to progress of adsorption in the emulsion. The character of agitation determines whether diffusion of the chemical through the oil to the interface has been accomplished and whether it has been sufficiently intensive and long to prepare the emulsion globules for coalescence.

In general, it is preferable to add the chemical "straight," or in solution in oil. When the compound is added as an aqueous solution, empirical adjustment of the strength and amount of solution is recommended. The water content must be reduced to the order of 1 to 2 per cent, and the chemicals may be used in varying proportions, usually very small, and sometimes as little as 1 part in 10,000 to 50,000, on the basis of recovered oil.

Temperature changes have great effects. Temperature controls almost every characteristic of an emulsion system, such as specific gravities of both components, viscosity of oil, activity and permanence of substances adsorbed in the interface, kinetic energy of the impacts caused by agitation, and altering the agitation itself. Temperature affects also the properties of the compound acting as a demulsifier.

The temperature to which the oil is heated is one of the most important factors in treating cut oil by the chemical method. The relation between percentage loss by volume and change in degrees A.P.I. for different crude oils (California and Mid-Continent) is presented in graphs in Fig. 25a. The data indicate that a volumetric loss of 2 to 3 per cent

per degree change in A.P.I. gravity applies to a large class of crude oils.^{468a}

There is a direct relationship between the treating temperature and the quantity of chemical required. Within certain limits the quantities of heat and chemical may be varied inversely, *i.e.*, more chemical is required

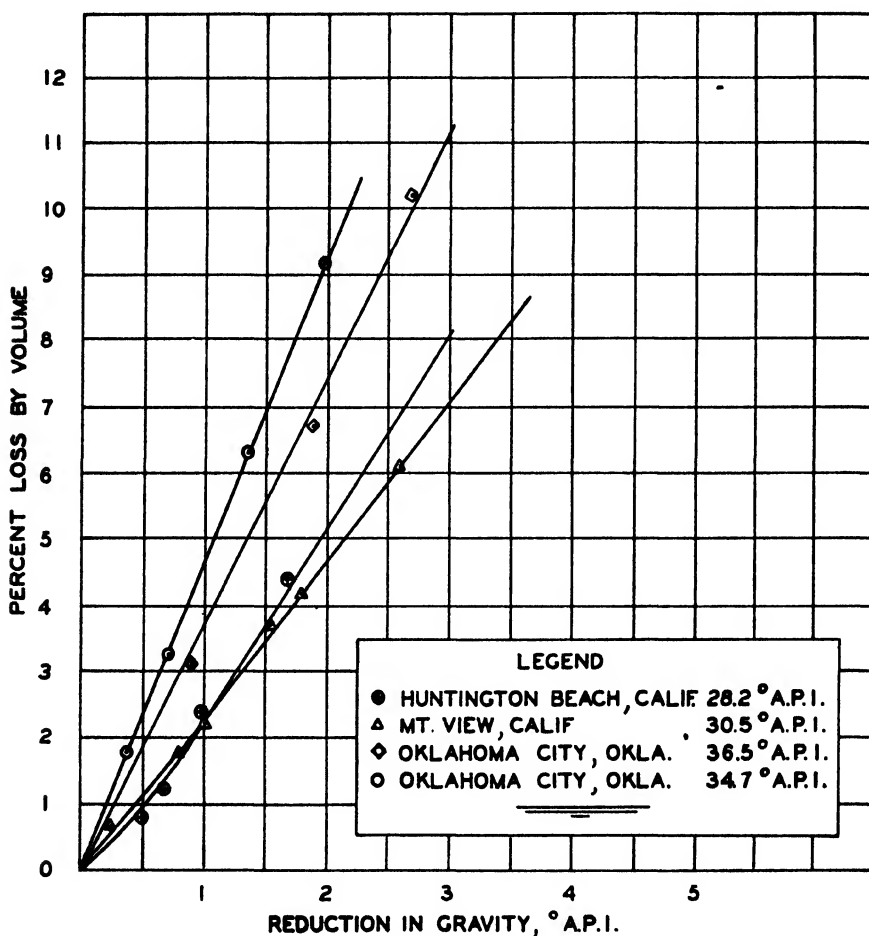


FIG. 25a. Relation Between Percentage Loss by Volume and Change in Degrees A.P.I. for Different Crude Oils.

at low than at high temperatures. As high temperatures are accompanied by the loss of the lighter fractions and a corresponding decrease in gravity and volume, it is often more economical to treat the oil at low temperatures and use more chemical.⁶⁴⁸

In an effort to determine the change in gravity and loss in volume due to heating an emulsion in the Seminole area, Oklahoma, engineers of a

large Mid-Continent oil company conducted laboratory tests to establish a gravity-volume-temperature relationship for the oil being treated. The tests showed that at temperatures below 120° F, there was no appreciable loss in volume or change in A.P.I. gravity, but that above 120° F there were losses in volume and changes in gravity. The loss in volume was 2.6 per cent per degree A.P.I. change in gravity.^{468a}

The results obtained in decreasing the treating temperatures in other areas likewise indicate that the cost of treating must be considered in terms of gravity, volume and chemical cost, instead of chemical cost alone. An optimum economic balance between A.P.I. gravity, volume losses, chemical and heat used can be obtained by treating the oil at the proper temperatures.

The effectiveness of chemical agents in resolving emulsions is considered by Roberts as a function of settling and separation of water; these are aided by low oil viscosity and large difference in specific gravity between water and oil. The viscosity factor may be controlled by heat, the degree of heat required being sufficient to lower the viscosity to or below 75-100 seconds Saybolt. The gravity differential is also a function of temperature; thus the temperature applied must be compatible with that required for the most favorable viscosity. Finally, Roberts considers suitable tank equipment for use in settling and separation of water, as well as gravity differential and viscosity, as a factor determining the effectiveness of resolving emulsions by chemical methods.

Acids, Bases and Salts

According to Bottars,⁵⁶ acids should be added for the disintegration of emulsions. The resolution of oil-in-water emulsions containing solid substances, if carried out with sulfuric acid, usually requires large proportions of acid (up to 5 per cent). If the emulsions are previously treated with solutions of salts of alkaline earths, such as magnesium or calcium chloride, the main amount of water separates and subsequent treatment with only about one-per cent sulfuric acid suffices to separate the sludge from the water-free oil.¹⁵³

A crude oil containing emulsified water and corrosive metallic salts is mixed with an aqueous solution of an alkali, such as sodium hydroxide or sodium carbonate, in an amount sufficient to convert the corrosive metallic salts into non-corrosive compounds; the mixture is heated to facilitate this conversion; and most of the water and non-corrosive compound formed are separated under pressure from the heated oil.³⁷¹

The demulsification of Baku crude oils is best performed by treating with sulfuric acid and neutralizing the acid with sodium hydroxide. Separation of the crude oil is best effected by passing it through tubular heaters. If the proper proportions of the reagents are used, the ash content of the oil stays within standard limits.⁷²

Kala crude oil emulsions are broken by the addition of one per cent of 25-per cent regenerated sulfuric acid at 50° C. The contacting period in the acid-treating equipment is 7 to 8 seconds. Sea water (20 to 30

per cent) is used to wash away the acid subsequently.^{70,71} The heavily emulsified Kala crude oil in Tzaritzin, used as boiler fuel, has been demulsified by admitting 0.5-per cent sulfuric acid and agitating with steam and air. The acidified water collects on the bottom of the storage tank and is constantly replaced by fresh water.²⁷⁰

Augustin,¹⁵ in his article "On the Emulsifying Power of Various Soaps," indicates as demulsifiers salts and electrolytes in general, such as potassium hydroxide, sodium hydroxide, potassium chloride, and sodium sulfate.

Fischer¹⁵⁵ breaks oil-in-water emulsions by intimate mixing with an aqueous solution of an electrolyte, *e.g.*, sodium carbonate. The emulsion is thereby converted into a water-in-oil emulsion, which is separated under the action of a high-voltage electric field.

Robinson⁴³⁹ treats lubricating oil stock with a large volume of diluted aqueous alkali solution, such as a 2-per cent sodium hydroxide solution, to form an oil-in-water emulsion; this results in separating the emulsion into a water and an oil phase.

Nugent³⁰⁵ investigated the demulsifying action of sodium hydroxide solution on emulsions of benzene-in-water containing 50 per cent by volume of benzene and not less than 0.1 per cent of gelatin as stabilizer. If sodium hydroxide is added immediately after the production of the emulsion, demulsification starts at once. If the emulsion is left undisturbed for some time prior to the addition of sodium hydroxide solution, demulsification does not occur for a period following the addition. The inhibition period seems to depend on the interval between the formation of the emulsion and the addition of sodium hydroxide. Nugent assumes that the stability increases because of the gradual formation of protective films around the benzene particles.

The Standard Oil Company recommends a soda solution treatment by neutralizing the acid oil with 18-20 Bé sodium carbonate solution, thereby decreasing its concentration by one-half. Sludging begins at a higher temperature. Nelson, Hallauer and Dons³⁶² treat emulsions with cellulose impregnated with sodium hydroxide by mild heating. Rapid resolution of the emulsion results.

Petroleum emulsions may be resolved by treating them with a solution containing 25 per cent of sodium hydroxide, 10 per cent of sodium acetate, 20 per cent of alcohol, about 10 per cent of glycerin, and the remainder water, all mixed well with sodium acid carbonate at 45-55°. In addition to dehydration, a far-reaching precipitation of salts suspended in the oil is obtained simultaneously.²⁸⁷

Benzene containing oil and fats in the form of an emulsion, may be clarified by saponifying the oil by means of an alkali solution. The benzene is injected in an atomized state into the alkali solution (sodium carbonate), to which sodium chloride is added to accelerate separation of the emulsion.⁶¹⁵

Gail and Adams¹⁰⁹ add iron chloride and sodium carbonate to destroy aqueous emulsions in a condenser. Barry⁸⁴ mixes the oil with sodium

chloride (one per cent by weight) and with 0.1-1.0 per cent of pulverized lime, heats the mixture and allows it to settle; resolution follows.

Cole⁹¹ worked out a method to break down water-in-oil emulsions by using metallic sodium and calcium chloride as demulsifiers.

Wagner⁶¹⁶ mentions an installation in Topila where calcium chloride is used for dehydration.

A combination chemical and heat treatment has been worked out by Born, Bonnette and Walker.⁵⁵ The process involves removing water from oil by gravity, treating the emulsion with a saline solution of about the same composition and salt content as that carried in suspension in the oil, and adding a small percentage of sodium hydroxide. The mixture is heated to 150-180° F. The oil and water separated are removed from the permanent emulsion and additional saline solution is added to the remaining emulsion.

Sherrick⁴⁷¹ also uses iron chloride as demulsifier to resolve emulsions; for example, to 200 cc of an emulsion a solution of 66.24 g of iron chloride in 100 cc of water is added. Separation of the emulsion into its components is the result of ion adsorption.

Herbsman²³⁰ recommends separation of oil and mineral salts from natural petroleum emulsions by mixing them with a highly concentrated solution of an emulsion-breaking reagent more soluble in water than are the mineral salts in the aqueous phase of the emulsion. The mixture is allowed to stand and to stratify; the oil layer is then withdrawn and delivered to storage, while the aqueous layer containing the reagent and the mineral salts, which is also withdrawn, is crystallized to recover the salts; the residual solution of the emulsion-breaking reagent is returned to the process for further use.

The amount of the oil-in-water dispersion in natural petroleum emulsions is usually very small. In certain areas, however, where the oil is of high viscosity and high specific gravity, or where the water accompanying it is relatively soft and fresh, dual emulsions are encountered. In these oil-in-water-in-oil emulsions the primarily dispersed water droplets themselves contain oil, *i.e.*, they are themselves emulsions in which oil is the disperse phase. The dual type emulsion water-in-oil-in-water may exist, but no practical attention has been paid to these systems. The oil-in-water type yields small recoveries of oil and is resolved by means of electrolytes such as calcium chloride, ferrous sulfate and hydrochloric acid.³⁴⁸

Solids

Separation of water from crude oil may be brought about by the addition of solid demulsifiers, coarse-grained materials, such as sand or glass, which assist in separating the water. Robinson⁴³⁶ brings a finely divided powder, such as granite dust, into intimate contact with the aqueous emulsion. The temperature is chosen so that one of the phases of the emulsion is agglomerated into a thick, solid mass to separate the other phase. The quantity of the solid added must be at least 20 per cent by

weight of the emulsion. A large proportion of the aqueous phase separates and then a further quantity of emulsion is added. When heated, the mixture undergoes a reversal of phases, and the resulting agglomerate of granite dust is settled and separated from the oily phase. Trent mixes the water-containing material with ground carbon-containing material to form a plastic mass which aids in removing the impurities originally bound, as well as the water. Dittersdorf¹¹⁴ resolves emulsions by mechanical action of fine-grained materials, *e.g.*, fine sand, glass splinters, or iron splinters. The heated emulsion is mixed with the fine-grained material by means of air or a stirrer, or in filters filled with these substances. Eddy¹²⁷ uses as a demulsifying agent powders of diatomaceous earth, acid-treated clay, or marble. They are blown with gas or air onto a filter plate, provided with openings which are too small to permit passage of the powdered demulsifier; thus the latter is deposited on the filter plate while the gas passes through. The deposited coating of emulsifier is wetted before the flow of gas through the filter plate is arrested, and then the emulsion to be broken is passed through the filter.

Robinson⁴³⁸ secures continuous separation of oil-water emulsions, in which water is the disperse phase, by passing through the emulsion a flocculating agent or a counter-colloid, such as dispersed lepidolite, phosgenite, quartz, garnet, and magnetic iron ore. The grains must have an adhesion tension with water which is greater than their adhesion tension with oil; the grains are collected and returned to the emulsion for redispersion.

Robinson^{439a} claims that petroleum oil emulsions may be broken by direct contact with a relatively large amount of a coarsely powdered solid or a relatively small amount of a finely powdered solid, such as bentonite or zeolite, both possessing an adhesion tension with the dispersed liquid which is not less than two and one-half times their adhesion tension with the continuous liquid of the emulsion. These powders are insoluble and chemically inert to all the constituents of the emulsion. The proportion of the finely powdered solid is controlled so as to produce resolution of the emulsion at the desired rate.

Cross⁹⁷ dehydrated emulsions by intimate mixing with bentonite, which is removed afterward. Blake-Smith⁵³ (Brown and Meinzer) effect the resolution of emulsions by first disturbing the equilibrium in the emulsion system by stirring and then adding quartz sand, bentonite and other zeolites, as well as metal sulfides, with continued stirring. Fischer¹⁵⁸ uses a continuous treatment of the emulsion with a mixture containing iron pyrites and quartz. Robinson⁴³⁹ resolves emulsions of the water-in-oil or oil-in-water type by adding melted aluminum oxide, hematite, cork, or wood readily wetted by light oil. The grains are taken either to the upper or to the lower part by the rotation of the drum containing the emulsion mixture and the dispersed treating agent.

Van Loenen³⁰⁷ resolves petroleum emulsions by treating the emulsion with granular solid material having sharp edges. A definite ratio between fine- and coarse-grained bodies is maintained. Van Loenen³⁰⁸ also

resolves crude-oil emulsions with granular solids contained in a horizontal rotating drum so constructed that the solids are distributed in the liquid. Manley and Knoss³²⁰ separate oil and water from petroleum emulsions by preheating the emulsion to a temperature sufficient to effect demulsification when mixed with a solid demulsifying agent, such as a filter aid. The resulting mixture is subjected to a thickening process whereby separation of the demulsified liquids and the demulsifying agent in the form of a concentrated suspension is effected.

Morrell³⁵¹ dehydrates mineral oil-water emulsions by suspending a finely divided metal, such as magnesium, aluminum, zinc, iron, tin, lead, nickel, chromium, or copper in the emulsion, thereby increasing the conductivity; a high-voltage electric current is allowed to act upon the emulsion as it passes between two electrodes; this results in water separation.

Petroleum emulsions of the water-in-oil type are broken by the action of a demulsifying agent consisting of floating calcium carbonate in a solution of soda and a soluble salt of an alkylated aromatic sulfo-acid, such as sodium isopropyl- β -naphthyl sulfate.⁵³⁸

Oil-in-water emulsions are dehydrated by treating them with a mineral easily wetted by oil and poorly wetted by water, such as magnetite and pyrite, and then treated with a substance readily wetted by water, but not by oil, such as quartz or silicate. A counter-current is produced and stirring performed. An arrangement is provided for introducing the dehydrating mixture.³⁹⁰

Liquids used for sealing purposes, substantially free from sulfonated hydrocarbon material, may be freed from emulsion-forming impurities such as metal dust and linseed oil by slightly heating the water-in-oil emulsion which has formed in use, and adding at atmospheric pressure a solution containing at least one per cent of soap and water glass. The mixture is then allowed to stand and separate into layers, water and impurities forming the upper layer.³¹²

Emulsions of the water-in-oil type are broken and the oil desalted by treating with a 0.05-0.5-per cent mixture of a compound containing an OCl radical, *e.g.*, calcium hypochlorite $[\text{Ca}(\text{OCl})_2]$ $\text{Ca}(\text{OCl})\text{Cl}$ called "bleaching powder," and a solid material containing soda, water, together with a stabilizer such as a soluble chromate. A dry organic acid may be added to advantage.²³⁷

Water-in-oil emulsions, such as those of crude petroleum, are first freed from most of the water which precipitates out spontaneously, and then heated, *e.g.*, in a heat exchanger to 200° F, and then conducted with a salt solution through a tower filled with finely divided inert material such as quartz sand. The salt solutions should be of the same or higher concentration than the salt content of the emulsion, namely, about 10-25 per cent. The demulsified oil and the solution are led off separately.^{78a}

Gases

Alexander³ uses a non-inflammable liquid of low boiling point and low specific heat with a specific gravity above that of water, for exam-

ple, dichlorethylene, tetrachlorethylene, carbon tetrachloride, or tetrachlorethane. This is passed in a liquid or a gaseous state through the adsorption or filtering device for removing the oily substances. Prior thereto, as much as possible is removed by a reversed vapor stream or by air. The solvent is recovered by distillation.

Walker's ⁶¹⁸ patent for dehydrating oils involves an agent which may be used in a gaseous form to facilitate direct contact with the total emulsion surface in the body of the oil. Formaldehyde as a gas is used as a dehydrating agent. The formaldehyde gas is generated by passing steam through formalin or by heating paraformaldehyde, the gas generated being carried into and distributed by steam through the oil containing the emulsion. The formaldehyde gas, admitted into the oil under pressure, with steam as carrying agent, assists in breaking the emulsion. When the mixture is actively stirred, the viscosity of the oil decreases and the surface tension of the water in the emulsion is decreased. Acetaldehyde may be used instead of formaldehyde, but its expense prohibits its use commercially. The action of formaldehyde in breaking oil-in-water emulsions, as presented by Walker, appears to be more of a physical nature than a true chemical reaction, since formaldehyde does not ionize in a water solution and therefore cannot neutralize the electrical charge of the disperse phase of the emulsion. It is thought that the formaldehyde gas acts rather as a catalytic agent in breaking down the emulsion.

Burwell ⁷⁸ treats water-in-oil petroleum emulsions with small but effective amounts of constituents of a mixture, obtained by the action of an oxidizing gas, such as air, on mineral-oil hydrocarbons at 155° and under superatmospheric pressure up to 350 lbs per sq in in the presence of manganese oleate (which promotes oxidation), until a definite amount of acidic compounds, soluble in the reaction mixture, is formed. The unsaponifiable oxidation products and the unoxidized oil are separated from the mixture, so that the mixture which acts as a demulsifier consists largely of saponifiable acidic oxidation products of hydrocarbons.

Lerch ²⁰⁷ resolves emulsions by heating and agitating them with an air stream at 190-200° F in the presence of salt water and/or a chemical treating agent.

Pure Oil Company ⁴²⁰ first passes sulfur dioxide into the emulsion, and then hydrogen sulfide. The emulsion is heated at 130° F for one and one-half hours.

For breaking petroleum emulsions, Herbsman ²³² recommends mixing hydrogen with the emulsion and activating it with metallic iron, cobalt, or nickel, or with the oxides, formates, acetates, oxalates, and tartrates of these metals. Hydrogen may also be produced in an emulsion by electrolysis or by the addition of alkali or alkaline-earth metals; in the latter cases hydrogen, being in a nascent state, is especially active.

Colloids

Dehydration may also be carried out by addition of colloids. Ayres²¹ adds to an emulsion a small amount of a material which is soluble in petroleum, but contains also a substance, such as starch, defined as a water-soluble protective colloid which is normally insoluble, but may be rendered soluble in oil by dissolving it in other substances. De Groote¹⁹⁰ uses solutions of substances containing highly colloidal, coagulescent soap-forming radicals. The Sharples Specialty Co.⁴⁶⁴ adds to the emulsion an organic reagent free from mineral substances. Those substances should have properties of hydrophilic emulsifying colloids. Gelatin and glues are also of use, opposing the influence of the emulsifying colloid dispersed in the oil. In the case of crude petroleum and petroleum emulsions formed by an acid treatment followed by washing with water, this method of dehydration finds advantageous application.

Saponin,⁵¹⁵ a hydrophobic colloid soluble in oil, is recommended as a treating agent in dehydration processes.

Raul⁴²⁴ dehydrates crude petroleum at an increased temperature, using molasses as a demulsifier. The mixture is filtered and allowed to settle. Molasses and water separate from the oil.

Soaps

Gray¹⁸⁶ prepared a demulsifying agent by mixing the oil with resin containing some free sulfuric acid, separating the oil from the resin, and partially neutralizing with alkali. The neutralizing residue is then drawn off completely and the demulsifier thus formed is washed. Tretolite Co.^{513a} breaks an emulsion by heating it with a resin derivative.

According to De Groote,¹⁹⁰ mixtures of an aqueous solution of sodium oleate, sodium resinate, ammonium oxystearate, or potassium sulfonaphthenate may be used, together with a solution of a salt such as sodium chloride or sodium sulfate. Stearolactone mixed with a solvent such as ammonium oleate, potassium oleate, or saponin, is recommended; a hydrophobic oil-soluble treating agent, such as naphthenic acids, resins, fatty acids, sulfonic acids, olive oil, flaxseed oil, and a liquid such as an aqueous solution of glycerin,⁵¹⁸ may also be used.

Dennhardt¹⁹⁹ leads the crude oil under pressure into a container having a stirrer, and the oil is subjected to pressure with addition of suitable demulsifiers, such as sodium oleate, sodium resinate, sodium silicate, and phenol. The method serves to destroy roily oil and "BS" of very stiff emulsions.

Water-in-oil emulsions, such as "roily oil" or "bottom settlements" are treated¹⁹³ with calcium cresolate, magnesium resinate, or other suitable substances which are water-insoluble, water-wettable, colloiddally dispersible, and free from a fatty acid radical. The second patent specifies passing petroleum emulsions through material, such as sand, composed of small particles separated by voids approaching capillary dimensions, and simultaneously subjecting the emulsion to electric dehydrating action.^{189,191}

A water-soluble salt of calcium, magnesium, strontium, or barium and sodium oleate in aqueous or alcoholic solution may be used as a demulsifier in separating oil-in-water emulsions.

Since sodium and ammonium soaps are hydrophilic, they are used for breaking oil-field emulsions. Sulfo-soaps are produced by sulfuric acid treatment of the vegetable oil before saponification. The presence of free glycerol is generally advantageous.²⁹⁵

Among demulsifying chemicals quite popular for removing water from petroleum emulsions are agents allowing the silt and sediment to precipitate along with the insoluble soaps formed.³² Tret-O-lite is the registered trademark (U. S. P. Office TM 161,052, applied to demulsifying chemicals marketed by the Tretolite Company (formerly Wm. S. Barnickel & Co.).

The composition of a Tret-O-lite compound given by Matthews and Crosby,³²⁶ i.e., sodium oleate, 83 per cent; sodium resinate, 5.5 per cent; sodium silicate, 5.0 per cent; phenol, 4 per cent; paraffin, 1.5 per cent, and water, 1 per cent, has been obsolete for many years. It was dyed with azerole green and added to the emulsion in amounts of 0.1-1.0 per cent by weight. The treating procedure described by Matthews and Crosby was to obtain an intimate mixture by agitation with air or natural gas. The breaking of the emulsion is hastened by heating to 150° F. There is no limitation to the permissible oil content of emulsions susceptible to treatment with Tret-O-lite. Many emulsions containing 2 per cent or less of water are chemically treated to meet pipe-line requirements of 0.5 to 1 per cent. Tret-O-lite is used in proportions of one part of chemical to 10,000 parts or more of recovered oil. Thus, if all the Tret-O-lite remains in the oil and is present to the extent of 0.01 per cent or less, then it is an amount too small to be capable of analytical determination and insignificant compared to 0.5-2 per cent of the residual brine content (1 part in 200 or more). Several hundred varieties of Tret-O-lite have been or are being sold.

Maksimovitch³¹⁸ describes experiments carried out with naphthenic acid soap, water glass, commercial soap, starch and Tret-O-lite for breaking emulsions in Khaduzhi. The best results were yielded by Tret-O-lite containing sodium oleate 80 per cent, phenol 10 per cent and water glass 10 per cent; the proportion used was 0.05 per cent on the volume of the emulsion. Tret-O-lite was successfully replaced with 2-3 per cent of alkali sludge from kerosene. Bennett⁴⁷ gave a tabulation of existing products of Tret-O-lite used as demulsifiers, including their composition. The latter is complex and not all components appear to be essential.

A water-soluble soap and cyclohexanol may serve as demulsifier for petroleum emulsions. Suitable mixtures are the water-soluble soap and cyclohexanol with an alkali compound of aldehydes or ketones; furthermore, castor oil may be admixed with the first two. The same effect is attained with mixtures consisting of a water-softening body and an ammonia compound of furfural, or ammonia compounds of aldehydes or ketones.^{475a}

Alcohols

Taranow and Twertzin⁵⁰⁵ mix the emulsion with about 1 per cent of amyl alcohol or a solution of the latter in acetone, and allow it to settle.

Tyler⁶¹¹ effects resolution of water-in-oil emulsions by adding 0.5 to 2.0 per cent of a mixture of alcohols containing C₄ to C₇ or above C₈, boiling point 100-210° F, insoluble in water, and formed by catalytic hydrogenation of carbon monoxide under high pressure and temperature.

Koetschau²⁷³ describes the demulsifying action produced by alcohols. He considers the importance of determining the maximum speed of phase separation, which is a function of particle size, viscosity and gravity differential, and the resistance to emulsification as a matter of interfacial adsorption.

Wayne⁶²³ claims as resolving agents for petroleum and other water-in-oil emulsions polyhydric alcohols, aliphatic aldehydes, or fatty acids rendered soluble by sulfonation or condensation with aromatic sulfonic acids or alkyl amines or both.

A polyvalent alcohol (aliphatic, aromatic, or of a mixed nature), which is esterified with a polyvalent acid and with a hydroxylated fatty body, may be used as demulsifier in resolving petroleum emulsions. Phthalic acid or phthalic anhydride is heated with glycerin for about 10 minutes to 150°; the product is then heated with an equal weight of castor oil to 250° for 20 minutes, to combine the free acid groups with the castor oil.⁶⁰¹

A process of treating crude petroleum emulsions for dehydration purposes involves intimately mixing with the emulsion a prepared reagent containing fermentation products of micro-organisms, but substantially free from such living organisms. To prepare the reagent, a carbohydrate solution such as maltose, lactose, potatoes, rice, etc., is fermented through micro-organisms contained in it, producing alcohols in the proportion of at least 8-16 per cent by volume, and to it is added a cyanogen salt in combination with a metallic base. The liquid from the solution is separated and used to mix with the crude petroleum emulsion.⁴⁸⁷

Bregeat⁶⁸ continuously washes the emulsion with solutions of phenol or cresol, or their hydrated derivatives, or of naphthols, aromatics, sulfurated compounds or their mixtures, with or without pressure.

Co. Générale d'Exploitation des Brevets et Procédés de Recuperation Brégeat Société¹⁷⁷ either subjects emulsions to a systematic washing with substances of the phenol series or their hydrogenation products, or with hydrogenation products of naphthols and naphthalenes, or mixes them with aromatic derivative products of sulfuric acid alone or in an optional mixture with each other. Either the emulsion or the washing liquid is heated.

Lewis³⁰¹ decomposes emulsions by precipitating out the colloidal ingredients by adding a phenol ester and a dissociating salt which contains low-valent cations and monovalent anions; such salts are, for example, tribasic sodium phosphate, sodium ferrocyanide, and sodium ortho-

vanadate. Aluminum sulfate, which promotes coagulation, may also be added.

Hydroxy- Derivatives

Lewis³⁰⁰ introduces into the emulsion a compound prepared from an ester of an aliphatic acid with a hydroxy- derivative of a polycyclic compound, such as 1-naphthylbutyrate, 1-naphthylpropionate, 1-anthryl-valerate, or 3-phenanthrylcaponate. Calcium hydroxide is added with stirring to bring the solution to a pH of 8.5 to 9.5 and, with continued stirring, an electrolyte, such as ferric chloride, is added to bring about coagulation.

De Groote¹⁹² patented the following dehydration treatment: the emulsion is first subjected to the action of a demulsifying substance, such as hydroxy-stearic acid, β -naphthol, ester of ricinoleic acid, etc., and then dehydrated electrically.

Tretolite Co.⁵¹⁹ also subjected the emulsion to the action of an agent which consisted of about 30 per cent of a hydroxymonocyclosulfoaromatic group and 20 per cent of a non-hydroxylated aromatic tar acid oil.

Tretolite Co.⁵³⁹ uses as a demulsifier hydroxyoctadeca-9,11-dienoic acid material of the formula type XTCOOZ in which X is at least one oxygen atom or at least one hydroxyl radical or an acid residue; T , an octadeca-9,11-dienoic acid residue, and Z an acid hydrogen equivalent. Tretolite Co.⁵⁶⁵ claims that water-insoluble hydroxylated fatty acids, suitable for demulsifying water-in-oil emulsions, are obtained by hydrolytic decomposition of fatty acid sulfates of the linseed oil type, blown with air or oxygen until substantial oxidation takes place (150°). De Groote, Wirtel and Keiser⁵⁷⁷ patented as a demulsifying agent a poly-keto fatty acid compound such as may be derived by pressure oxidation of castor oil with linseed oil, methyl alcohol, and naphtha solvent. Another patent⁵⁷⁸ relates to similar use of a keto fatty acid material such as may be derived from castor oil with benzene and ethyl alcohol.

Another demulsifying agent⁵⁶⁰ is a hydroxylated non-sulfo-fatty acid compound of the type $(\text{R}'\text{TOH})\text{COOZ}$ in which R' is a fatty acid or its glyceride; T , an aromatic residue attached directly to R' ; OH , a hydroxyl attached directly to T ; COO , the carboxyl residue, and Z , the "hydrogen ion equivalent," such as the triethanolamine salt of phenol stearic acid.

An acid-free keto fatty acid compound, such as ketohydroxy-stearic acid or a salt or ester thereof, is used as demulsifying agent in breaking petroleum emulsions of the water-in-oil type. Similarly the use of a demulsifying agent consisting of a salt-free poly-keto fatty acid compound, such as may be derived from castor oil by suitable oxidation, has been suggested.⁵⁸⁰

The water-in-oil type of emulsion may be resolved by subjecting it to the action of a demulsifying agent characterized by the presence in the molecule of at least one radical obtained by dehydroxylation of a hydroxylated fatty acid compound, at least one radical obtained by elimination of at least two carboxylic hydrogen atoms of a polybasic car-

boxylic acid, and finally at least one amine radical, characterized by having in place of at least one amino hydrogen atom, a substituent radical obtained by dehydroxylation of a radical selected from the class consisting of polyhydroxyalkyl and polyhydroxyalkyl-oxyalkyl radicals. Further, the molecule is characterized by the fact that there is present at least one ester linkage involving one of the hydroxyl radicals of the polyhydroxy amine component.^{194a}

Condensation Products

De Groote and Adams¹⁹⁵ treat petroleum emulsions by subjecting them to the action of an altered hydrocarbon, a condensation derivative product (*e.g.*, starch treated with sulfuric acid and condensed with phenol). In this product the hydrocarbon group stands in a simple genetic relation to the starting material and contains an organic substance (the alkaline-earth salt, which is insoluble). Tretolite Co.⁵²⁵ patented the treatment of petroleum emulsions with condensation products of petroleum sulfonation products with aldehydes or ketones.

Rost⁴⁴⁴ claims a rapid separation of the emulsion when effected by the addition of 0.3 per cent of formaldehyde or its polymerized derivatives. This method may be applied in treating aqueous liquids, as well as fats, of every kind.

Tretolite Co.⁶⁰⁰ recommends breaking water-in-oil emulsions by means of a condensation product of a heterocyclic compound and a non-sulfo reactive hydrocarbon compound (which product may be saponified to render it water-soluble if a carboxyl group is present).

A demulsifier for water-in-oil emulsions may be made of the partial esterification product of a monocarboxy- detergent-forming acid, such as rosin acid, naphthenic acid, or higher fatty acids, and the dihydroxy-compound obtained by condensing urea with a number of molecular proportions of an alkylene oxide, such as ethylene or propylene oxide. The compound so obtained is treated in such a manner as to introduce a ricinoleyl radical. For example, 14 parts of a condensation product from urea and ethylene oxide are heated with 2.4 parts of stearic acid at 160° while stirring, until a sample of the mixture is completely soluble in water. The condensation product itself is prepared from a mixture of 1 part of urea with 30 parts of ethylene oxide heated in a closed, pressure-resisting container at 120° for 9 hours; 90 per cent of ethylene oxide entered into combination.⁵⁵¹

Organic Acids and Their Salts

Johnson²³⁹ demulsifies tar emulsions by the addition of a carboxylic acid, which is soluble in the tar but not in the water; resin, oleic, stearic, palmitic, linoleic, or arachic acids may be used.

Johnson and Birger²⁶⁰ treat aqueous tar emulsions with a water-soluble carboxylic acid soluble in tar. The product is allowed to stand until separation occurs.

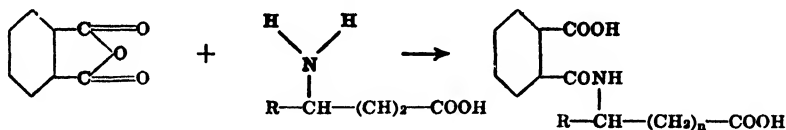
Schmidt's⁴⁵³ demulsifying and dissolving medium consists of the

water-soluble salts of carboxylic acids, substituted by higher aliphatic radicals, such as propyl, butyl and amyl. An example is butyltetrahydronaphthalenecarboxy acid which, when added to Tetralin, gives a clear solution on dissolving in water.

Hinrichs²⁴¹ mixes emulsions with a solution of a chlorine addition product of a liquid fatty acid in carbon tetrachloride, and Bloxam⁶⁴ treats the emulsion with a kind of modified fatty acid, ethers and sulfonates of fatty acids. Further, sulfurated fatty acids and their derivatives, hydroxylated, halogenated, sulfurated and nitrated products, as well as amines, ethers and soaps are used.

The numerous chemical compounds used for breaking crude-oil emulsions may or may not be of the water-softener type. Some fatty acid compounds, similar to sulfonated oil or Turkey-red oil, act on the colloidal matter in resolving the emulsion.

Petroleum emulsions may be resolved by adding a fatty acid derivative of coconut oil,¹⁹⁴ and also by the use⁵⁷⁰ of amino fatty acids obtained by treatment of unsaturated fatty acids or unsaturated fatty acid glycerides with ammonia or organic primary or secondary amines, such as butyl-, amyl-, ethanolcyclohexylamines, aniline, or piperidine. The amino group may be replaced by, or exchanged with a second molecule of unsaturated fatty acid. Also, the amino fatty acids may be converted with anhydrides of dibasic carboxylic acids, such as succinic or maleic acids or phthalic anhydride, for example:



Pyhala,⁴²¹ discussing the dehydration of emulsified crudes of Bibi Eibat near Baku, as well as of Tschaleken Island in the Caspian Sea, points out that some of these emulsions could not be broken at all. Berkahn⁴⁸ succeeded in dehydrating these crude emulsions by adding kerosene naphthenic acids. Addition of 0.5 per cent of a naphthenic acid gave satisfactory results. (This method has been patented in Russia.) Gurwitsch, and later Naphtali, explained the dehydrating action of naphthenic acids by the decrease of interfacial tension; but they considered normal emulsions consisting of water and oil without foreign substances, whereas the stiff emulsions are those containing mostly free petrol acid, and a considerable proportion of mineral ingredients distributed in a mechanical combination. Berkahn, in his patent, considers that naphthenic acids cause solution of by-products which act as stabilizers. In the crudes concerned such a stabilizer seems to be ozokerite. (A decrease in the interfacial tension also follows by the addition of petrol acid and kerosene, as well as of naphthenic acids, because they dissolve the stabilizer.) Similarly, the stable emulsion state of crudes not containing paraffin is destroyed by the addition of naphthenic acids. In this case

the naphthenic soaps play the part of the stabilizer. The alkaline water forms salts of petrol acid which, being replaced by metallic salts present in the water, are converted into soaps. The latter separate because they are insoluble in water and are adsorbed by the crude oil, being readily soluble in it. Under certain physical conditions favoring the formation of an emulsion, *e.g.*, when the crude oil is mixed with water, lime or sand by means of natural gas under pressure, the soaps mentioned above precipitate out and mix with the earth sludge and water, and a stable crude emulsion is formed.

Ryazanovskii⁴⁴⁹ states that addition of a solution containing 0.25 per cent of naphthenic acids and 0.25 per cent of sodium chloride, or 0.25 per cent of naphthenic acids and 0.2 per cent of sodium hydroxide effects a 98.6 per cent separation of oil from water.

Conversion of esters of fatty acids, resin acids, naphthenic acids or their halide derivatives, or of sulfo compounds with polyvalent alcohols containing free OH groups with sulfuric acid, whereby the free OH groups are saturated by each mol of sulfuric acid, yields products which may serve as demulsifiers. The remaining hydrogen atom of sulfuric acid may be saturated further by alkali, ammonia, or organic nitrogen bases, such as pyridine. A suitable compound is obtained by preparation of an aromatic sulfo fatty acid by condensation of ricinoleic acid with phenol in the presence of sulfuric acid. The acid sodium salt of this sulfo acid is esterified with glycerin chlorhydrine and finally converts the reaction product with pyridine sulfuric acid; $C_{17}H_{33}-HC_6H_3(OH)(SO_3Na)-COO-C_3H_5(OH)-SO_4H-C_5H_5N$ ⁵⁴⁸ is obtained.

Petroleum emulsions are resolved by means of esters obtained by esterification of oxy-fatty acid amides with polybasic acids, such as succinic, maleic, fumaric, citric, oxalic, tartaric, glutaric, naphthenic or sebazinic acid. The oxidation products of ricinoleic acid, cottonseed oil, oleic acid, and corn oil are used most frequently as oxy-fatty acids. The acid groups of the demulsifier so obtained may be neutralized with alkalis or organic bases. The amides of fatty acids or oxy-fatty acids, such as ricinoleic acid amide, oxyricinoleic acid amide, oxystearic acid amide, dioxystearic acid amide, and polyricinoleic acid amide have also been specified as demulsifiers for petroleum emulsions.⁵⁷¹

The acid esters of strong, polybasic carboxylic acids, such as citric, fumaric, maleic, oxalic, and phthalic acids, with monovalent aliphatic alcohols, such as butanol, amyl alcohol, and propanol, are used for breaking petroleum emulsions. The acids should show a dissociation constant above 7.10^{-4} at 18-25°. Monobutyl phthalate is especially suitable.⁵⁵⁰

Tretolite Co.⁵⁸⁵ used a mixed ester, such as the reaction product of mono-olein with oxalic acid, or one⁵³¹ derived from castor oil, phthalic anhydride, and glycerol as a demulsifier. Halogenated polyvalent alcohols may be substituted for glycerol, and oleic acid, stearic acid, naphthenic acid or resin acid for castor oil. Tretolite Co.⁵⁹⁸ claims as demulsifier a reaction product obtained from one mol (356 lbs) of mono-olein (oleic acid and glycerol) heated with one mol (118 lbs) of finely pulver-

ized succinic acid; the mixture is stirred and dry air is blown through it at 185-200° until an ester is formed. Abietic or naphthenic acid may be used instead of oleic acid; polyhydric aliphatic, aromatic, cyclic, or heterocyclic alcohols for glycerol; and maleic, citric, tartaric, or fumaric acid for succinic acid.

Kuczynski²⁸⁶ added 0.1-0.3 per cent of commercial carbolic acid for dehydrating emulsions. The temperature maintained is about 40°. Above 100° a smaller proportion of the chemical, 0.01 per cent, is sufficient. Separation time for 10,000 kg of the emulsion is about 12 hours. Steam economy and minimal benzine wastes are claimed for this method.

Averill^{17,18} patented several methods for the dehydration of emulsions by means of chemicals. He added water,¹⁷ varying from 5 to 80 per cent by volume, to the original emulsion in order to re-emulsify it, after which he subjected it to the action of a demulsifier. An amount of water at least equal to the volume of the emulsion, is added. The mixture is demulsified with a chemical agent which causes all the water to separate. Furthermore, the same investigator¹⁹ proposed heating the emulsion before adding the demulsifier, subjecting it to electric dehydration after homogenization, and settling it by gravity. It is suggested that a demulsifier, β -naphthol ester of ricinoleic acid, be added to the emulsion, which is then subjected to homogenization, to diminish the distribution of sizes of water droplets formed, and finally dehydrated electrically. An apparatus for dehydration by means of chemical reagents is described by Averill in another patent.¹⁸

Tretolite Co.⁵⁶² effects demulsification by using dehydration products of ricinoleic acid of a specified character, such as are formed by heating ricinoleic acid above 100°, neutralizing with a substituted basic amine, such as triethanolamine, and diluting with pine oil. A mixture of blown fatty material, such as blown castor oil, and alkylated naphthalene sulfonic acid compounds in specified proportions is recommended. Tretolite Co.⁵⁶³ refers to the use of a demulsifying agent composed on an ester derived from a non-cyclic, non-fatty, dibasic carboxylic acid of the type $(CH_2)_n(COOH)_2$, in which n is at least 5 and not more than 8, and a hydroxylated fatty acid compound, such as sebacic acid, castor oil, or the like. Tretolite Co.⁵⁶⁴ discloses a demulsifier comprising a hydroxyhendecenoic acid material of the formula type $xTCOOZ$, in which x is at least one oxygen atom or at least one hydroxyl radical, or an acid residue; T , a hendecenoic acid residue; and Z , an acid hydrogen equivalent.

Tretolite Co.⁶⁰² breaks petroleum emulsions by using neutral phthalyl mono-olein as a demulsifying agent.

Another demulsifier which has been used is a mixture of ammonium ricinoleate and addition compounds of $KHSO_3$ with aldehydes or ketones, such as butylaldehyde, crotonic aldehyde, aldol, benzaldehyde, furfural, acetone, methylethylketone, or methylisobutylketone. Especially suited is a mixture of 11.1 per cent furfural $KHSO_3$, 50.4 per cent ricinoleic acid, 8.9 per cent NH_3 (26° Bé) and 29.6 per cent castor oil.⁴⁷⁵

Tretolite Co.⁵⁸² uses as demulsifiers acetylated products of hydroxyl-

ated fatty acids, *e.g.*, the ammonium salt of the sulfo acid of acetylricinoleic acid. For example, 400 parts of castor oil and 200 parts of acetic anhydride are boiled in a reflux condenser for four hours. To the cooled product is added 200 parts of 60° Bé sulfuric acid with stirring; it is allowed to stand for 24 hours, and washed with water or sodium sulfate to remove the excess acid. The product obtained contains acetyl sulfo ricinoleic acid, $\text{CH}_3(\text{CH}_2)_5\text{CH}(\text{CH}_3\text{COO})\cdot\text{CH}_2\text{CH}(\text{SO}_4\text{H})(\text{CH}_2)_8\text{COOH}$, which is neutralized with alkali.

Tretolite Co.⁵⁵⁸ breaks petroleum emulsions with a demulsifying agent composed of a substituted triricinolein in which three "alcoholform" hydroxyls have been replaced by radicals, such as those of oxalic or phthalic acid, in which the hydrogen of the carboxylic radical may be replaced by NH_4 to form a salt.

Another agent used in breaking petroleum emulsions⁵³⁵ consists of a mixture of: (a) a water-soluble sulfo material, such as triethanolamine salt of dioxalyl-triricinolein, which has demulsifying properties but does not precipitate, when free from other materials, in the presence of an alkaline-earth salt; and (b) a water-soluble demulsifier, such as the sodium salt of sulfonated oleic acid, which forms a precipitate with alkaline-earth salts. The constituents (a) and (b) are used in proportions corresponding to their average molecular weights, and the combined mixture is capable of being wholly precipitated by alkaline-earth salts.

A demulsifying agent for treating water-in-oil emulsions is obtained from a castor oil ricinoleic acid, polyricinoleic acid, or the like by heating to about 150-200° and blowing with air or oxygen for 15-20 hours. Likewise polyketo acids may be used having the type formula $[\text{CH}_3(\text{CH}_2)_5\text{COCH}_2\text{R}(\text{CH}_2)_7\text{CO.T.COO}]$, in which *R* represents the grouping $-\text{CH}=\text{CH}-$ or $-\text{CH}(\text{OH})\text{CH}(\text{OH})$ and *T* represents a fatty acid radical obtained by subjecting castor oil mixed with linseed oil (not over 10 per cent) to oxidation at approximately 45 lbs pressure and at about 120°.⁵⁸¹

Another invention regarding oil-demulsifying processes pertains to the use of a reagent composed of an aqueous solution of alkali thiocyanate or alkali thiosulfate and a diethylene glycol ether. A typical reagent may be prepared by mixing one pound of sodium thiosulfate and 2.43 lbs of diethylene glycol and adding 41.6 lbs, or approximately five gallons, of water. Small percentages of lactic and acetic acids may be added if desired.⁴⁸⁸

Emulsions of the water-in-oil type are broken with a demulsifying agent containing in the same molecule an oxyhendecadiene acid residue and an oxyoctadecadiene acid, such as a diglyceride or ethylene glycol derivative. The octadecadiene acid is obtained by splitting off water from ricinoleic acid. For the preparation of the demulsifier, both acids are oxidized with air at 125-135° at about 3-5 atmospheres, and are likewise simultaneously esterified with glycerin. Both acids may also be sulfurized and the product hydrolyzed. A demulsifying agent having in the same molecule an oxyhendecenoic acid residue and a keto fatty acid

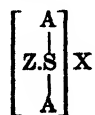
residue derived from castor oil may also be used. In preparing this demulsifier, a keto fatty acid, obtained by the oxidation of ricinoleic acid, is added to each molecule of oxyoctadecadiene and heated with glycerin or ethylene glycol, whereby complete esterification occurs. Another patent relates to the use of demulsifying agents containing a dicarboxy acid residue $(\text{CH}_2)_n(\text{COOH})_2$ in which n is 5, 6, 7, or 8 in mol compound with an oxyhendecenoic acid residue. The temperature used for the preparation is 125-135°. Esters obtained by the esterification of dioxyhendecenoic acid glycerin ester with pimelic, suberic, azelaic, or sebacic acids may be used as demulsifiers.⁵⁴⁴

Petroleum emulsions may be resolved by a demulsifier obtained by the reaction of oxyhendecenoic acid with a base such as an amine, *et al.*, having the general formula YTCOO.Z , in which Y is at least one oxygen atom or at least one OH radical; T is the hendecenoic acid residue $\text{C}_{10}\text{H}_{19}$; COO is the conventional carboxyl residue, and Z is an acidic hydrogen equivalent, such as an organic radical, a metal, or an amino group. In preparing this demulsifier, 148 parts of phthalic anhydride are heated with 92 parts of glycerin for 10 minutes to 125-180° until all free glycerin disappears, the product containing free hydroxyl groups. Into this product are introduced 218 parts of dioxyhendecenoic acid and the mixture is heated for 10-30 minutes to 150-250°, cooled and diluted with 10-50 per cent denatured alcohol. The free acid still present is neutralized by an organic amino base.⁵⁴⁵

A compound comprising both an oxyoctadecadiene residue and a dicarboxy acid residue derived from an acid, such as sebacic acid, of the type formula $(\text{CH}_2)_n(\text{COOH})_2$ in which n is 5, 6, 7, or 8, is used as a demulsifying agent in breaking water-in-oil emulsions. Another patent relates to the use of a demulsifying agent containing both a keto fatty acid residue derived from castor oil and a dicarboxy acid residue as mentioned above. In still another patent, a demulsifier of the general formula $(\text{R.COO})_m\text{T}(\text{OH})_m$ is used in which R.COO represents a non-sulfo detergent-forming monocarboxy radical; T , a polyhydric alcohol residue, such as glycerol or ethylene glycol glycerin; m , the number one, or more; and R and T are from extraneous acid residues. Finally, heptioic acid esters with oxy-fatty acids such as ricinoleic, oxyhendecenoic or oxyoctadecadiene, may serve as demulsifiers.⁵⁴⁶

In treating emulsions, particularly those from wells, a demulsifying agent comprising a product obtained by a mild, gaseous oxidation of a chemical compound, such as diphthalated mixed triglycerides from diricinolein and fatty acids of linseed oil mixed with drain oil from coal tar and oxidized with air at 75°, is used.⁵⁵¹

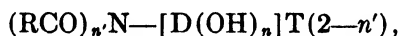
Water-in-oil emulsions may be broken by the use of a cation-active, surface-active substance of the type formula:



in which *Z* represents any univalent aliphatic hydrocarbon radical having at least 12 and not more than 22 carbon atoms; *A*, a substituent hydrocarbon radical to replace a hydrogen atom of the sulfonium radical (the total number of carbon atoms present in *AAZ* is not over 35); and *X*, a propyl sulfuric acid radical.^{557-I}

Petroleum emulsions of the water-in-oil type are subjected to the action of trimethyloctylphosphonium propyl sulfate or other cation-active, surface-active substance of the formula *ZAAAPX*, in which *Z* represents any univalent hydrocarbon radical having at least 6 carbon atoms; *AAA* is at least one hydrocarbon radical, and not more than 3 hydrocarbon radicals which replace three hydrogen atoms of the phosphonium radical (these hydrocarbon radicals are univalent, bivalent or trivalent hydrocarbon radicals, provided the total valence value of *AAA* is 3); and *X* represents a non-surface-active radical or component. The total number of carbon atoms in *AAAZ* is not over 35.^{557-II}

Another demulsifying agent which may be used is a reaction product of ricinoleic acid with diethanolamine, phthalic anhydride and glycerol or another compound of the general type formula *YX* in which *Y* denotes a residue derived from an amide of the formula:



in which *n* and *n'* represent the numerals one or two; *D* is a hydrocarbon radical; *T* is a non-ionizable hydrogen atom equivalent selected from the class consisting of a hydrogen atom, a univalent hydrocarbon radical and a hydroxylated hydrocarbon radical containing not more than two hydroxyl radicals; *RCO* is the acyl radical of a detergent-forming carboxylic acid; and *X* is a residue derived from a polybasic carboxylic acid of the type *B(COOZ)_{n''}*, in which *n''* denotes a numeral at least as great as 2 and no greater than 3; *B*, the polybasic carboxylic acid residue; and *Z*, an ionizable hydrogen atom equivalent.^{557-III,IV}

Another patent ^{557-V} relates to a similar use of demulsifying agents of the general formula: (*X*) *RTD*, where *R* represents an aromatic nucleus; *X*, an alkyl radical having at least 3 and not more than 16 carbon atoms; *T*, an aliphatic hydrocarbon radical containing not more than 30 carbon atoms attached directly to *R* by means of a carbon atom to *C* atom linkage; *D*, a radical selected from the class consisting of hydroxyl radicals, carboxyl radicals, sulfonic acid radicals, amino groups, and quaternary ammonium radical; and *n*, the numerals 1, 2, 3, 4; *R* is additionally characterized by being free from any other substituent.

In the preparation of such compounds, 150 parts of sulfuric acid are converted with 68 parts of phenyl acetic acid at 50-60°, to which is added 148 parts of *n*-butanol or isohexyl alcohol and 300 parts of sulfuric acid; the mixture is stirred for 2-15 hours; 75 parts of hydrocinnamic acid are dissolved in 148 parts of *n*-butanol and reacted with 275 parts of sulfuric acid at 50°. Triisobutylhydrocinnamic acid is obtained. By using larger amounts of butanol, more butyl groups are introduced into the hydro-

cinnamic acid forming, for example, tetraisobutylhydrocinnamic acid. Butylated phenyl-*n*-valeric acid is obtained from phenol-*n*-valeric acid, which in turn is obtained from phenol-*n*-valeric aldehyde (obtained from cinnamic aldehyde and maleic acid with additional dehydrogenation and decarboxylation) and *n*-butanol. Butylated naphthyl acetic acid is formed in a similar manner, i.e., 34 parts of phenyl acetic acid are dissolved in 84 parts of *n*-dodecylene, 18 parts of water are added and condensed with boron fluoride at 60°. Triisobutylphenyl acetic acid chloride is reacted with sodium oxyethansulfonate. Benzene sulfonic acid is reacted with propanol to tri- and tetrapropylbenzene sulfonic acid and triethylbenzylammonium chloride is butylated with *n*-butanol and sulfuric acid. Cymene is reacted with ethylene glycol chlorhydrine, whereby the hydrocarbon is split off and the residue C_2H_4OH substituted. Through the reaction of amylated naphthalenes with glycerindichlorhydrine, products are obtained in which the chlorhydrine group is substituted either in the amyl group or direct in the naphthalene nucleus. These products are coupled with sodium oxyethansulfonate; thus either the sodium or the hydrogen of the OH group reacts with the chlorine of the chlorhydrine group present.^{557-V}

Another demulsifying agent is a high molecular weight polyether carboxylic acid compound containing an acid radical, characterized by (a) derivation from an aliphatic polyhydric alcohol containing 2-4 carbon atoms; (b) the presence of at least one hydrocarbon radical having at least 8 carbon atoms, and being of an aliphatic cycloaliphatic, alicyclic or aralkyl nature; (c) attachment of the hydrocarbon radical to an ether radical containing at least one of the hetero atoms, the linkage still being through the hetero atom; and (d) the presence of at least 2 etheric oxygen atoms and by not more than 3 alkylene-oxy radicals directly attached to each other. For example, diethylene glycol monododecyl ether is fused with phthalic anhydride for 2-3 hours at 140-150°, the cooled product dissolved in alcohol, neutralized with sodium hydroxide or potassium hydroxide, and the resulting product employed in demulsification.

Sulfonated Compounds

Hey²³⁹ describes a dehydration process in which the precipitation of impurities is effected by mixing intimately with impure hot oil or a cold solvent containing one of the following substances or a mixture of them: sulfonated oils, aqueous or alcoholic solutions of sulfonated oil soaps of potash, soda or ammonia. The sulfonated oil is produced by the action of strong sulfuric acid upon oleic or ricinoleic acid or their glycerol esters, or olive or castor oil, either separately or mixed together, and diluted with a hydrocarbon solvent, such as benzene, toluene, xylene, naphtha, or mixtures of them. The surface tension of the finely divided water is decreased and it settles out by gravity from the oil or the solvent, producing a clear liquid and leaving a sludge containing all the foreign matter, as well as the excess of the reagent used.

In another patent the petroleum emulsion to be dehydrated is mixed

with a substance⁵²⁴ consisting of cresol and sulfonated oil with a considerable amount of oxystearic acid. The mixture is allowed to stand to separate the water from the oil. Instead of oxystearic acid, a considerable amount of sulfo-oleic acid⁵²³ may be added. The petroleum emulsion may be resolved by mixing it with a condensed product of a fatty substance (oleic acid) and a non-hydroxylated sulfonated aromatic substance (benzene, toluene, xylene, etc.), as well as with another complex compound. The emulsion to be dehydrated is treated with a mixture of a compound of cresol and a water-soluble salt of sulfonated castor oil.⁵²²

Tretolite Co.⁵⁶¹ breaks water-in-oil emulsions by the action of a demulsifying agent composed of equal quantities of water-miscible and oil-soluble petroleum sulfonate sodium salts and drastically oxidized castor oil, mixed with about 10 per cent of kerosene. Fischer and Reddish¹⁶⁰ state that crude-oil emulsions may be decomposed by using a reagent comprising a mineral oil sulfonate and ethyl alcohol. Rogers⁴⁴¹ breaks emulsions of mineral oil and water by adding the sodium salt of a sulfonated mineral oil ($\frac{1}{4}$ to 4 lbs per barrel of the mixture), applying heat. According to the Standard Oil Development Co.,⁴⁰⁴ mineral oil emulsions separate water by the addition of a water-soluble sulfonic acid. The sulfonic acid is obtained by the action of strong sulfuric acid upon a mineral oil. The amount added is up to 5 per cent and the product is heated to about 165° F. A sulfonated product of a partially hydrogenated fat, such as castor oil or cottonseed oil, may serve as a demulsifier.⁵²⁷

Petroleum emulsions may be treated for the purpose of breaking with a polymerized, blown and sulfonated product derived from a vegetable oil, such as cottonseed or corn oil.⁸⁷ Tretolite⁵⁷⁶ prepared a demulsifier for petroleum emulsions by mixing 500 parts of coal tar (anthracene oil, specific gravity 1.1), and distilling at 250-400° with 250 parts of oleic acid. The mixture is sulfonated with an equal volume of 66° Bé sulfuric acid at 35°. The product is washed and neutralized with ammonia to the methyl orange end point. Singer⁴⁷⁶ demulsifies petroleum emulsions by adding pine oil to the extent of 10 per cent to the usual demulsifier, containing sulfonated oils, whereby the viscosity of the demulsifiers is decreased at low temperatures. A petroleum emulsion may be broken by agitation with a mixture of water-miscible and oil-soluble sodium salts of sulfonated petroleum, 45 per cent, blown castor oil 45 per cent, and kerosene 10 per cent.⁴² Halloran²¹⁰ adds to the emulsion five per cent by volume of a product obtained by sulfonating kerosene with concentrated sulfuric acid and heating the mixture to 79° C.

The mechanism of the sulfonation process is described by Michael and Weiner.³⁴⁵ Separating oils from their emulsions with water is achieved by adding not more than 5 per cent by weight of a sulfonic acid solution in water formed by the action of concentrated sulfuric acid or oleum on a petroleum lubricating oil.⁴⁰⁴

Naphthenic acids, resins, fatty acids, sulfonic acids, olive oil, flaxseed, etc., and a liquid such as an aqueous glycerin solution, may be used successfully in demulsification processes.⁵¹⁶

Bukh, Pivovarova and Mirzoeva⁷⁴ obtained a successful separation of oil from water by introducing up to 1 per cent of "black contact" (sulfonic acids) at a temperature of 90-95° C, or even lower. The interaction between the sulfonic acids and calcium naphthenates results in the formation of oil-soluble calcium sulfonates, and thus assures the breaking of the emulsion. The application of "black contact" should be effected with great care because of the corrosive action on the apparatus. Bukh and Mirzoeva⁷⁵ break Bibi Eibat emulsions which cannot be settled at 80° C without the use of reagents. It is suggested that an acid sludge of unknown composition should never be used in breaking an emulsion. The "contact" and the acid sludge obtained in the sulfonation of kerosene ("black contact") are best, the latter being preferred because of its cheapness. The treatment requires only 20 to 30 minutes, and the entire operation requires about one hour. The use of the kerosene acid sludge instead of the heavy acid sludge previously mentioned does not affect the acidity of the crude oil more than in the first case. The loss of gasoline is prevented by using a closed treating apparatus.

Petrow⁴⁰⁶ separates emulsions by splitting fats and oils using aromatic sulfo-acids, such as those of naphthalene and octohydroanthracene, etc. When 0.1-0.5 per cent of calcium sulfate is added to the splitting substance, the sulfonic acid separates as a salt from the glycerin, water and fatty acids.

Tretolite Co.⁵²⁸ proposed as an oil-soluble demulsifier a mixture of (1) petroleum sulfonic acid soluble in water but insoluble in oil, free from polymers and of naphthenic-base crude oils of the Gulf Coast obtained by a repeated acid treatment; and (2) naphthenic acids or their salts with a mean molecular weight of 225. The emulsion may also be treated⁵²⁹ with a 10 per cent solution or suspension of a demulsifier which is a mixture of (1) hydroxylated fatty acid (molecular dispersion), and (2) a water-soluble alkali salt of an alkylated naphthalene sulfonic acid, prepared with an alcohol having not less than three and not more than five carbon atoms, *e.g.*, the ammonia salt of a butylated naphthalene sulfonic acid. The two components of the mixture are mixed in the ratio 1:3. Tretolite Co.⁵³⁰ also recommends as a demulsifier a mixture made up of (a) 13 to 60 parts of a salt of an oil-soluble petroleum sulfonate and a partially saponified, modified fatty acid product in the ratio 4:1 or 1:4; (b) 4 to 30 parts of a dilute alcohol and kerosene in the ratio 1:5 or 5:1; and (c) 1 to 5 parts of ammonium sulfate.

Coggeshall and Reilly⁸⁹ separate emulsions, especially from crude petroleum, by vigorous stirring with an aromatic or aliphatic sulfo-acid or its salt, followed by the addition of an alkali or an alkaline-earth salt solution. For example, a solution of one part of an aromatic sulfo-acid and 9 parts of water is stirred with 500 parts of emulsion, to which is added 7.5 parts of sodium chloride in a 20 per cent water solution. Water separates on standing. The sulfo-acid may be replaced by soaps; therefore one part of the sulfo-acid is replaced by 2 parts of soap. In the case of difficultly separable emulsions, the mixture is heated to 70-75° F.

Petroleum emulsions containing impurities were broken by mixing with fatty sulfonic acids; the impurities and precipitated water³³ were thus separated. Kontol Company²⁷⁵ developed a method of breaking petroleum emulsions which involved adding a mixture of a water-soluble mineral sulfo-acid and a fatty sulfo-acid and heating to 150-200° F.

De Groote, Keiser and Wirtel¹⁹⁸ bring about demulsification by adding a sulfonic derivative of an unsaturated fatty substance, in which SO_3H is attached to a carbon atom not adjacent to the original ethylene linkage. Thus oleic acid is treated with sulfuric monohydrate at 35° C and the hydrogen sulfate produced is sulfonated, hydrolyzed and neutralized with NH_4OH .

A demulsifying agent⁵⁶⁷ comprises a sulfo- compound derived by sulfonation of an unsaturated acid body, produced by thermal decomposition of an unsaturated oxy-fatty material, *e.g.*, a salt or ester of sulfo-hendecenoic acid.

Rogers⁴⁴¹ adds a sodium sulfonate to a "BS" emulsion of mineral oil and water at the rate of $\frac{1}{4}$ to 4 pounds of salts per barrel of oil, and maintains the mixture at an elevated temperature until separation into layers occurs.

For demulsification of Kalinsch's petroleum, a contact containing sodium sulfonates (0.1 per cent) was used at 30° for 15 hours. Higher temperatures greatly accelerate separation of the emulsion.⁷² Likewise, neutralized acid goudron proved to be a satisfactory demulsifier requiring a temperature of 40° for demulsification; it does not cause any corrosion.⁷⁴

Walker⁶²⁰ resolves emulsions by the addition of sulfo-oleic acid, oleic acid and stearylactone, or by using a demulsifying agent⁶²¹ comprising a mixture of reaction products resulting from the sulfonation of equal proportions of benzene and commercial oleic acid.

Tretolite Co.⁵⁶⁰ breaks petroleum emulsions of the water-in-oil type by using as a demulsifying agent sulfoaryl esters of higher aliphatic or naphthenic acids, which may be modified by the addition of a double linking or an acylation of the hydroxyl group (0.2-0.005 per cent). For example, the desired product is prepared by heating 490 parts of sodium sulfobenzylricinoleate with 148 parts of phthalic anhydride in xylene at 120-130° C.

A mixture of sulfo-oleic acid, oleic acid and stearylactone is suggested as a demulsifying agent for breaking oil-in-water emulsions. For breaking a water-in-oil emulsion, sulfonation and condensation products from equal amounts of commercial benzene and commercial oleic acid are added to the emulsion.⁶⁰⁶

De Groote⁵³³ recommends, as agents for breaking water-in-oil emulsions, compounds having the general formula $\text{KTZSO}_3\text{R}'$, where *K* is an aromatic residue from benzene, phenol, toluene, xylene, naphthalene, naphthol, methyl naphthalene, anthracene, or phenanthrene; *T*, hydrogen, chlorine, the hydroxyl group, etc.; *Z*, an acidic hydrogen equivalent, such as sodium, potassium, magnesium, nitrogen, or triethanol, and *R'* a

reactive hydroaromatic residue, *e.g.*, cyclohexanol, methylcyclohexanol, or a cyclohexene derivative. These agents are taken in ratios from 1:500 to 1:30,000, preferably 1:10,000, if the temperature used is up to 93° C. A suitable agent may be prepared from 130 parts of naphthalene, 100 parts of cyclohexanol, and 400 parts of sulfuric acid (66° Bé), reacted and washed with 500 parts of water. The upper, oily layer, after separating, is neutralized with strong ammonia water. A resolving agent⁵³⁴ is obtained from a sulfo-compound of a fatty acid treated with sodium hydroxide, potassium hydroxide or ammonium hydroxide, or esterified, such as oleic acid or ricinoleic acid, obtained by treating these in an ether solution of chlorosulfonic acid. Diethyl sulfide, glycol, or butyric acid may be used instead of ether, and pyrosulfuric acid may be substituted for chlorosulfonic acid.

Tretolite Co.⁵³⁶ breaks water-in-oil petroleum emulsions by using a substituted ester of the general type $R''\text{COO}(\text{TSO}_3\text{Z})$, in which R'' is a fatty acid radical; T , an aliphatic residue; Z , an acidic hydrogen atom of the sulfonic acid or its equivalent, with (TSO_3Z) replacing the carboxylic hydrogen, such as a soluble ammonium salt of the hydroxyethane sulfo-ester of phthalylricinoleic acid.

Herbsman²²⁹ treats water-in-oil emulsions with a mixture of a sulfonated glyceride (50 per cent) and an alkaline-earth salt, such as magnesium chloride (up to 20 per cent) dissolved in a homolog of benzene, an alcohol, a phenol, or a hydrocarbon solvent (30-50 per cent).

Limburg³⁰² breaks water-in-oil emulsions by the addition of an aqueous solution of a resinous condensation product from an aldol and an amide of a carboxylic acid, formaldehyde and a sulfonated phenol oxymethylene, a polyhydric alcohol, an unsaturated fatty acid and an aromatic dibasic acid or a sulfonated anhydride, or by the addition of a phenol aldehyde compound and an aromatic sulfo- acid.

Tretolite Co.⁵⁹⁰ recovers oil from petroleum emulsions by using a demulsifying agent derived from the chemical reaction of a hydrocarbon containing an abietine nucleus, such as abietine, an aldehyde, such as formaldehyde (40 per cent), and a sulfonating agent.

Petroleum emulsions⁵²⁶ may be resolved by using as a demulsifier a sulfo- derivative of lauryl alcohol obtained by the action of sulfuric acid (66° Bé) upon alcohol at 35° C. In another Tretolite Co. patent,⁵⁸⁸ the emulsion is treated with a demulsifier containing a sulfonated hydrocarbon with twelve to twenty-four carbon atoms in the alcohol molecule, representing a sulfo-acid derivative or a sulfuric acid ester. Cetyl sulfonic acid is suitable.

De Groote, Monson and Wirtel⁵⁸⁴ claim as a demulsifying agent one containing a substituted aromatic detergent-forming sulfonic compound of the type $X\text{FRSO}_3\text{Z}$, in which X denotes a polycyclic aromatic nucleus; F , a detergent-forming organic residue; R , a residue of an alcohol containing less than twelve carbon atoms and substituted in the aromatic ring; and Z , a hydrogen ion equivalent.

Tretolite Co.⁵³⁷ prepares a demulsifier from a mixture of 30 parts by weight of the sulfonated product of a polymerized terpenic hydrocarbon; 60 parts by weight of pine oil and 10 parts by weight of neutralized sulfonated castor oil. Tretolite Co.⁶⁰¹ breaks petroleum emulsions of the water-in-oil type by subjecting them to the action of a demulsifying agent which is a reaction product derived from phthalic anhydride, glycerol, castor oil and the like, or the sodium or ammonium salts of such products.

As demulsifying agents are claimed: (1) the sulfonated condensation product of a hydroaromatic alcohol, such as cyclohexanol, with an aromatic hydrocarbon, preferably polycyclic, *e.g.*, $C_{10}H_8$; (2) a Cl-sulfonic acid produced by action of $ClSO_3H$ and Et_2O on oleic acid; (3) an alkylated arylsulfonic acid, ligninsulfonic acid, sulfonated fatty acids, higher alkyl sulfates, the $N(C_2H_4OH)_3$ salt of dioxyalyltriricinoleine and (4) sulfonic acid derivatives of ricinoleic acid, such as the β -sulfoethyl esters of ricinoleic acid, ricinoleyl phthalate, or its glyceryl esters.¹⁹⁹

Petroleum emulsions of the water-in-oil type are subjected to treatment with a demulsifying agent comprising a sodium salt of sulfosuccinic acid dihexyl ester, or various compounds of the general formula $ZO_2.CCH(SO_3Z)CH_2CO_2Z$, in which Z represents an ionizable hydrogen atom, a metallic atom, an ammonium radical, or an organic radical obtained by dehydroxylation of an alcoholic hydroxyl-containing compound.⁵⁶⁹

Compounds of the structure $\begin{matrix} R \\ | \\ R > CO \end{matrix}$, where R is an aliphatic residue having 11 to 22 carbon atoms and containing one aromatic sulfo-acid, such as the compound $[C_{17}H_{34}(OH)(C_6H_3NaSO_3)]_2CO$, serve as demulsifiers for petroleum emulsions. This compound is obtained by treating $(C_{17}H_{33})_2CO$ with sulfuric acid and further subjecting it to condensation with phenol sulfo-acid at about 30-35° (not above 40°). Likewise, the condensation is assisted by the introduction of sulfur trioxide. The keto-sulfo-acid is soluble in water and neutralized thereafter with alkali or organic bases.⁵⁴⁹ A substance comprising a sulfite addition product derived by reaction between a water-soluble sulfite, such as sodium acid sulfite, and an unsaturated reactive fatty material, such as linseed oil, serves as a demulsifier.⁵⁴⁰ De Groote¹⁹³ used a substance comprising wood sulfite liquor material and a sulfonic demulsifying substance, such as propylated naphthalene sulfonic acid, as a demulsifying agent.

A process for breaking a petroleum emulsion of the water-in-oil type has been described as follows. The emulsion is subjected to the action of a demulsifying agent comprising a non-cyclic bisulfite addition product of a non-carboxy aldehyde obtained by thermal decomposition of an oxy-unsaturated fatty body. The demulsifier may comprise likewise the bisulfite addition product of a non-carboxy aldehyde obtained by thermal decomposition of ricinoleic acid. The demulsifying agent may be a heptoid aldehyde addition product having a formula of the following type: $C_6H_{13}CH(OH)SO_3Na$, or $C_6H_{13}CH(OH)SO_3K$, or $C_6H_{13}CH(OH)SO_3NH_4$.⁵⁷³

Many methods for dehydration with chemicals have been patented in which emulsions are heated with esters of naphthenic acid.⁵¹⁷ Naphthalene sulfo-ricinoleate, sulfo-oxyanthracene resinate¹⁹⁶ and the alkaline-earth salt of a sulfonated mineral oil^{513b} have been used as demulsifiers. The emulsion⁵²¹ may be treated with a sulfonated aromatic hydrocarbon compound, benzene, toluene, phenol, anthracene with an hydroxylated acid, hydroxylated resin, naphthenic acid, stearic acid, and a complex organic compound obtained by treatment of a hydroxylated fatty acid and a sulfonated aromatic hydrocarbon substance with a dehydrating agent.

Tretolite Co.⁵¹⁴ treats petroleum emulsions with a mixture of a condensation product of a sulfonated aromatic compound, a soap-forming acid and another organic compound, which is obtained by sulfonation of a fatty acid and an aromatic compound in which the ratio of the aromatic molecules to the fatty acid molecules is larger than 1:1. The emulsion may be subjected to the action of a mixture of condensation products of a sulfonated aromatic hydroxypolycyclic compound (α or β -naphthol dihydroxynaphthalene, hydroxyanthracene⁵²⁰).

Walker⁵¹⁹ claims demulsification of water-in-oil emulsions or the prevention of their formation in petroleum refining by the addition of sulfonated polynuclear aromatic compounds and an aliphatic alcohol condensation product, such as diisopropylnaphthalene sulfonic acid.

De Groote and Adams¹⁹⁷ used condensation products for the destruction of emulsions. These consist of two soap-forming radicals combined with a sulfonated polycyclic aromatic body.

Resolution of emulsions⁵⁸⁶ may be effected by a demulsifier containing naphthenic acids, its salts, or its esters having a molecular weight between 200-575 and an average molecular weight of 225, and distilling between 230 and 310°. In another patent Tretolite Co.⁵⁸⁷ uses as a demulsifier a mixture consisting of (a) about 40 per cent water; (b) a water-soluble ammonium salt of a sulfo- compound of an alkylated naphthalene with at least three, and not more than five, carbon atoms; and (c) a naphthenic acid or its salts with a molecular weight between 200-575. The ratio of the mixture is: b:c = 1:3 or 3.1. A 20 per cent solution in benzene is formed. As an alternative⁵⁸⁸ for (c) of the above mixture, oleic acid alone, or saponified partially by alkali, ammonia, or triethanolamine, may also be used. Emulsion resolution⁵⁸⁸ occurs by treating with a demulsifier prepared from an ammonium salt of a butylated naphthalene sulfonic acid, and about the same amount of a petroleum sulfonic acid, soluble in oil and water, partially neutralized with ammonium hydroxide and diluted with kerosene. The demulsifier⁵⁸⁹ may consist of a mixture of not more than 40 per cent water and equal amounts of a dialkyl polysulfonate produced from gas tar and a naphthenic acid with a mean molecular weight of 225 and a boiling range between 230-310°.

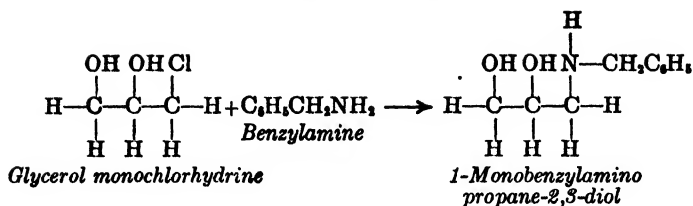
Cyclohexyl-amino salts of alkylated naphthalene sulfonic acid, such as mono-, di-, or tri-isopropylnaphthalene sulfonic acid, the alkyl groups

of which contain 3-10 carbon atoms, may be used as demulsifiers for the resolution of petroleum emulsions. In the preparation of alkylated sulfonic acids, naphthalene sulfonic acids are substituted for the corresponding alkyl sulfuric acids, such as methyl-, ethyl-, propyl-, isopropyl-, butyl-, amyl-, hexyl-, octyl-, and decyl-sulfuric acid in the presence of an excess of sulfuric acid.⁵⁷⁵

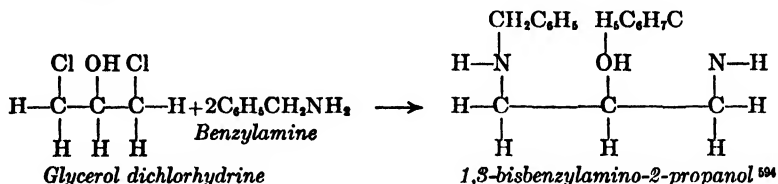
Another patent⁵⁴⁷ relates to the use of a demulsifying agent containing a substance produced by sulfonating an alkali-soluble condensation material obtained by reaction between an alkylene oxide material such as ethylene oxide, etc., and a resinous material derived in part from a phenol such as a phenol aldehyde condensation product. Demulsification of water-in-oil emulsions may be effected by using as demulsifying agent an alkylated naphthalene sulfonic acid compound in the form of a sulfonated amine salt. The substituted amine is of the kind obtained by reaction between an amine of the formula H_mX_nN , in which m and n are each 1 or 2 and their sum is 3, and X is an alkyl, cyclohexyl or aralkyl residue, and a mono- or di-chlorhydrine derived from glycerol, a glycerol ether, a glycol, glycol ether or its equivalent, such as ethylene oxide, higher alkylene oxides, glycidol, or the like (the naphthalene nucleus being replaced by at least one alkyl group containing 3-10 carbon atoms). An especially suitable demulsifying agent is obtained by converting naphthalene into its mono-sulfonic acid and isopropyl alcohol into the acid sulfate, combining these two products in the presence of sulfuric acid as a condensing agent, washing and separating the aqueous waste acid, neutralizing the sulfonic acid with 1-cyclohexyl-amino-2,3-propanediol, and adding a suitable solvent.⁵⁹¹

Alkylated naphthalene sulfonic acids containing in their alkyl groups 3-10 carbon atoms and neutralized with substituted aliphatic amines with 4-8 carbon atoms may serve as demulsifiers. The substituted amines in their turn are obtained through conversion of the corresponding amines with chlorhydrine of ethers of polyvalent alcohols, such as glycol or glycerin.⁵⁹² In the process of breaking petroleum emulsions of the water-in-oil type, it is suggested using for dehydration a substituted cyclohexylamine salt of an alkylated naphthalene sulfonic acid in which at least one alkyl group substituted in the naphthalene nucleus contains 3-10 carbon atoms, the substituent of the cyclohexylamine radical being a hydrocarbon radical. Especially suitable is the diethylcyclohexylamine salt of triisopropylated naphthalene (mono) sulfonic acid.⁵⁹³

Alkyl-substituted naphthalene sulfonic acids, in the form of a polyhydric alcohol-substituted phenyl alkylamine salt, are claimed as very effective demulsifying agents for the dehydration of petroleum emulsions. These substitution products are obtained by conversion of halide compounds of polyvalent alcohols with phenylalkylamines, for example, mono- or dichlorhydrine of glycerin or glycol with benzylamine, or glycidol, ethylene oxide or polyglycols or glycerins with benzylamine. The reaction between glycerol mono-chlorhydrine and benzylamine is given as illustration:



Likewise the reaction between glycerol dichlorhydrine and benzylamine is as follows:

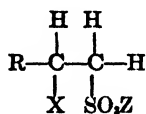


Another compound for breaking petroleum emulsions is a demulsifying agent comprising an alkylamino propanol salt of an alkylated naphthalene sulfonic acid, in which at least one alkyl group substituted in the naphthalene nucleus contains not less than three nor more than ten carbon atoms, e.g., the amylamino propanol salt of a butylated naphthalene monosulfonic acid.⁵⁹⁵

Breaking of petroleum emulsions is carried out by using as demulsifiers salts of alkylated naphthalene sulfonic acids, which contain as basic component condensation products obtained from aliphatic alcohols (mono- and polyvalent alcohols, glycidol) with primary or secondary amines, such as piperidine. Condensation products obtained by conversion of halogen hydrines with the amines are: 1-monoamylaminopropane-2-3-diol, 1-diamylamino propane-2-3-diol; 1,3-bisamylamino-2-propanol; 1,3-bisdiamyl-2-propanol.

Similarly, alkylated naphthalene sulfonic acid, neutralized by oxyalkylalkylamine or oxyalkyldialkylamine obtained by conversion of glycol-chlorhydrine or ethylene oxide with 1 or 2 mols of alkylamine or dialkylamine may be used. The chlorhydrine of butylene-, propylene-, amylene-, hexylene-, heptylene-, nonamethylene-, decamethylene-, undecamethylene-, tridecamethylene-, tetradecamethylene-, or octadecamethylene-glycol may be used instead of glycolchlorhydrine.⁵⁹⁶

The reagent to be used in breaking petroleum emulsions may consist of a sulfonated hydrocarbon obtained by reacting an aliphatic unsaturated hydrocarbon, containing at least 8 carbon atoms and having a double bond at the end of the chain, with a strong sulfonating agent. In general, the demulsifying agent comprises a chemical compound of the type formula:



in which R—C—C represents the aliphatic chain having at least 8 carbon atoms; X is an ionizable acid residue derived from acids such as phosphoric, sulfuric, or boric, as well as halogen hydrides and water-soluble fatty acids, and Z, an ionizable hydrogen atom equivalent. The demulsifier may be in the form of a water-soluble amine, such as alkylolamine, or a triethanolamine salt, comprising the type formula⁵⁰⁵ shown above.

The demulsifying agent may consist of a chemical compound obtained by treating an aliphatic unsaturated hydrocarbon, containing at least 8 carbon atoms (up to 30 carbon atoms) and having a double bond at the end of the carbon chain, with a strong sulfonating agent in such a manner that it takes up a sulfo- group, and treating the sulfonation product with a hydrolyzing agent. For example, 30 parts of a mixture consisting essentially of 1,2-hexadecylene or 1,2-octadecylene with 20 parts of chlorosulfonic acid are stirred vigorously and kept cold for 3 hours. The reaction liquid is treated with water, then neutralized with 20 per cent sodium hydroxide solution and 6 parts excess of sodium hydroxide added. The carbon tetrachloride is steam-distilled off and recovered, the residual liquid boiled 30 minutes and neutralized with 10 per cent sulfuric acid. An immiscible oil which forms in the mixture is separated and the aqueous solution evaporated to a thick reddish brown oil, soluble in water.⁵⁵²

Aromatic oxysulfonic acids, especially their amino salts, containing in the nucleus an aliphatic residue with 13-30 carbon atoms, *e.g.*, the cyclohexylamino salt of cetylphenol monosulfonic acid or the amylamino salt of cetylnaphthol sulfonic acid, may serve as demulsifiers for petroleum emulsions. These compounds may be obtained by reacting waxes, wool wax, beeswax, carnauba wax, flax wax with phenol, cresol, naphthol, heating with zinc chloride, aluminum chloride, or the like, then sulfonating and neutralizing the product.⁵⁵³

The treating or demulsifying agent to be used in a process for breaking petroleum emulsions may comprise an alkylated naphthalene sulfonic acid in the form of a polyamine salt, in which at least one alkyl group substituted in the naphthalene nucleus contains 3-10 carbon atoms, and the neutralizing salt-forming amine is characterized by the type formula: $\text{NH}_2 \cdot \text{C}_2\text{H}_4 (\text{C}_2\text{H}_4\text{NH})_x \text{NH}_2$, where x is a whole number less than 20. The tetraethylene pentamine salt of propylated naphthalene monosulfonic acid admixed with a suitable solvent is especially applicable. Likewise, an alkylated naphthalene sulfonic acid in the form of a polyamine salt, in which at least one alkyl group substituted in the naphthalene nucleus contains 3-10 carbon atoms and is neutralized by an amine of the type formula $(\text{C}_2\text{H}_4\text{NH})_x \cdot \text{C}_2\text{H}_4\text{NH}$ (where x is a whole number greater than one and less than 20) may be used as a demulsifying agent. The triethylenetriamine salt of propylated naphthalene monosulfonic acid admixed with a suitable solvent is especially recommended.⁵⁵⁴

Resolution of petroleum emulsions may be obtained by using as demulsifiers products obtained by strong sulfonation of olefins with more than 8 carbon atoms, especially 1,2-olefins, such as 1,2-hexadecylene or 1,2-octadecylene. A sulfonation agent is considered to act more strongly

than concentrated sulfuric acid, and the products obtained may be esterified with triethanolamine or may be neutralized with inorganic or organic bases. On the other hand, oxybenzene sulfo-acids with acyl residues having 8-40 carbon atoms in the benzene ring may be utilized as demulsifying agents. The products are obtained by condensation of spermaceti oil with phenol in the presence of zinc chloride at about 185°, followed by sulfurization of the cetyl phenol mixture with a small amount of palmityl phenol. If carnauba wax is substituted for spermaceti oil, arylphenol is obtained by condensation with palmityl phenol, and the mixture may be separated by vacuum distillation. The acids obtained may be further esterified or neutralized with triethanolamine. Furthermore, the use of sulfonation products of phosphatidene, such as lecithin, which have been neutralized, has been suggested. The sulfonation is carried out in a solution of tri- or per-chlorethylene at about 1-10°. ⁵⁵⁵

The demulsifying agent proposed for use in breaking petroleum emulsions may consist of a sulfonic acid derivative of an acylated aromatic compound of the kind in which the acyl group has at least 8 and not more than 40 carbon atoms. Such materials are prepared preferably by sulfonation of an acylated aromatic body. In general, the demulsifier comprises a chemical compound of the type formula: $[\text{OH.T(D)}].(\text{SO}_4\text{Z})$, in which *T* is a monocyclic aromatic residue and *D*, a ricinoleyl radical nuclearly substituted; and *T* and *Z* represent an ionizable hydrogen atom equivalent or an organic radical, a triethanolamine radical, an alkylolamine radical, a substituted ammonium radical, or a metallic atom equivalent. ⁵⁵⁶

A process for breaking petroleum emulsions involves subjecting the emulsion to the action of a demulsifier comprising a sulfonation product derived from a phosphatide, a vegetable lecithin,, a soybean lecithin in the form of an ester, an acid, a salt, an amino salt, a water-soluble amine, or a triethanolamine salt. ⁵⁵⁷

Tretolite Co. (de Groote ^{557a}) effects resolution of petroleum emulsions with compounds obtained by esterification of polyvalent alcohols containing sulfo- groups with polyvalent carboxylic acids, as well as with carboxylic acids containing monovalent oxy- groups. The products obtained are used especially in the form of their amino salts. Suitable products are also obtained by conversion of: (1) one mol of anhydrous glycerin sulfo-acid triamylamine with one mol of acid butylphthalate; (2) two mols of acid amylphthalate; (3) one mol of sodium isoäthionate with one mol of phthalic anhydride followed by esterification with one mol of castor oil, mono-olein, mono-abietine, stearyl alcohol, fatty acid amide, or oxyethyltoluenesulfonamide; (4) by condensation of anhydrous sodium glycerin sulfonate with sodium isoäthionate and esterification as in example 3, or with oleic acid, naphthenic acid, abietinic acid, or acetic acid; (5) by conversion of the sulfo-acids from mineral oil refining, the so-called "green acids" or "mahogany acids," with phosphorus pentachloride to sulfo-chlorides and esterification with glycerin, so that in the molecule two OH groups remain free, whereby further esterification is carried out

as before; and (6) similar esterification for monobutyl- β -naphthalene sulfonic acid chloride. Diglycerin may be used instead of glycerin, maleic acid or its anhydride for phthalic acid, and di- or trihydric for monohydric.

Products obtained by the esterification of oxy-fatty acids or their glycerides with polybasic carboxylic acids, followed by neutralization of the acid esters with amines which are substituted at the nitrogen atom by oxy- groups carrying alkyl radicals, may be used as demulsifiers.

De Groote also patented as demulsifying agents those substances produced by esterification of an alkylol aromatic sulfonamide with a polybasic carboxylic acid compound, *e.g.*, phthalic anhydride, oxalic acid, or maleic anhydride. In the preparation of this demulsifier, for example, 215 parts of *n*-monooxyethyl-*p*-toluenesulfonamide or 260 parts of *n*-di-*p*-toluenesulfonamide are reacted at 200° with 148 parts of phthalic anhydride. Oxalic or maleic anhydride, instead of phthalic anhydride, may be used for the conversion, whereby the reaction temperature may be reduced to 140° or 108°. Xylenesulfonamide, naphthalenesulfonamide, or amyl-naphthalenesulfonamide are formed in a similar manner.^{557-VII}

A propylated butylated cyclohexylamino salt of naphthalene sulfonic acid, or any other suitable cyclohexylamine salt of a polyalkylated naphthalene sulfonic acid containing at least two different alkyl groups, each of which has 3-10 carbon atoms, may serve as a demulsifying agent for petroleum emulsions. Likewise, the cyclohexylamine salt of an alkylated naphthalene monosulfonic acid in which at least one alkyl group contains 3-10 carbon atoms, such as a butylated or an amylated compound, may be used.^{575a}

Wayne⁶²² resolved petroleum emulsions by subjecting them to the action of demulsifiers consisting of amino or imino derivatives of nuclear-substituted aromatic sulfo- compounds. These emulsifiers were prepared by condensing aromatic sulfonic acids replaced in the nuclei by one or more residues from aldehydes, ketones, alcohols, or fatty acids with aromatic amines. It was found that amino or imino groups attached themselves directly to the benzene nucleus. The demulsifying action of these agents is attributed to the formation of colloids by the condensation of aromatic sulfonic acids with aromatic amines. The new treating agent is appreciably soluble in the water, as well as in the oil phase. Therefore penetration into the water/oil boundary is made possible.

Petroleum sulfonic acids and their alkyl-substituted derivatives are also considered suitable for the resolution of emulsions. Highly colloidal condensation products of dialkyl-naphthalene disulfonic acid, aniline, toluidine, or diphenylamine have also been proposed.³¹³

A demulsifying agent⁵⁴³ of the general formula: $Z.NC_6H_5.X$, in which *Z* represents any aliphatic hydrocarbon radical having 8-26 carbon atoms and *X*, a non-surface-active negative radical or component, such as cetyl or octadecyl pyridinium bromide, may be used for breaking petroleum emulsions. Cetyl pyridine bromide is obtained by heating 31 parts of cetyl bromide with 8 parts of pyridine at 140-150° until a sample

solidifies on cooling. Likewise, another patent recommends using as emulsifier the sulfocarboxylic amide compound of the general formula:

$R-CO-N < \begin{matrix} Y \\ R'.T.Z \end{matrix}$, in which $R-CO$ represents the acyl radical of a carboxylic detergent-forming acid (abietinic or naphthenic acid); Y , a hydrogen or an alkyl radical; R' , alkyls; T , the SO_3 or OSO_3 group; and Z , an acidic hydrogen or its equivalent, such as the sulfonation product of oleic acid ethyl anilide.

Condensation products of cyclic sulfonic acids with alkyl-, aralkyl-, or cycloalkyl amines may serve as demulsifiers. The cyclic sulfonic acids are obtained by sulfonation of naphthalene, anthracene, and their hydrogenation, chlorination, or alkylation products, *e.g.*, by means of chlor-sulfonic acid. Likewise, sulfurization products of the corresponding oxy- compounds or of pyridine or quinoline may serve as initial substances for condensation. Among the amines especially suitable are those with three or more carbon atoms. With regard to the aralkyl amines, the amino group should be present in the alkyl side chain. It is stated that condensation products are more active than the alkali salts of the corresponding sulfonic acids.⁶²⁴

A demulsifying agent for petroleum emulsions may be prepared by mixing sulfuric acid with glacial acetic acid, sulfonating unsaturated hydrocarbon polymers extracted from cracked petroleum distillates with the mixed acids, and neutralizing the resulting product.^{420a}

Blown Oils

Fuchs¹⁶⁸ separates water-in-oil emulsions by adding to them a saponified blown oil dissolved in ethyl alcohol and diluted with water. Tretolite Co.⁶⁰³ claims the formation of a demulsifying agent by the super-oxidation of blown castor oil at 200° in the presence of air, oxidation being continued until a product of semi-livery consistency is obtained.

Another Tretolite Co.⁶⁰⁴ patent refers to a demulsifying agent consisting of an anhydrous mixture, oil-soluble at least in high concentrations, comprising blown oil compounds such as those obtained from castor oil (15-50 per cent), one or more acid salts of a sulfo- fatty acid, such as an acid sodium salt from sulfonated castor oil (2-15 per cent), an unsaponified sulfur-free fatty acid derived from the sulfonation of a material such as castor oil, followed by hydrolytic decomposition, with the splitting off of sulfuric acid (20-60 per cent), and an aliphatic monohydric alcohol, such as isopropyl alcohol (2-25 per cent).

Petroleum emulsions may be resolved by means of an unsaponified demulsifying agent containing an aldehyde carboxylic acid residue. Likewise, an unsaponified blown fatty oil, such as castor, corn, or rape oil, may be used. The petroleum emulsion may also be treated with the reaction product of a blown fatty oil and an aldehyde reactive reagent, such as that produced from ammonia gas and blown castor oil.⁹⁰

Water-in-oil emulsions may be broken by applying chemical treatment, using a demulsifier such as is obtained by the esterification of free

hydroxyl groups of castor oil with oxalic acid, or their alkyl or halogen substitution products. For example, 100 parts of castor oil are heated to 110° with 28.5 parts of water containing oxalic acid, passing carbon dioxide through the mixture until di- and tri-esters are formed, and then treating at 145° until no free oxalic acid is present and the product has a molecular weight of about 1850.⁵⁵⁹

The treating agent used in breaking petroleum emulsions may consist of a blown (oxidized) oil which has been saturated by the action of a labile additive reagent, followed by a reaction in which the latter is removed in such a manner as to leave the product completely or almost completely saturated. For example, a blown castor oil derivative having an iodine number of less than 20 is derived from castor oil which has been treated by a sulfuric acid compound capable of entering into addition reactions; with subsequent removal of the sulfuric acid compound, the derivative may be mixed with a suitable solvent.⁵⁷⁴

Demulsification of water-in-oil emulsions may be effected by using as demulsifiers oxidation products of castor oil obtained by oxidation at 125-165° under a pressure up to 70 atmospheres. These oxidation products are diluted with an equal amount of kerosene and a weak organic base, such as triethanolamine, enough of the latter being used to neutralize the acids formed by oxidation.⁵⁷⁹

A mixture composed of 15-20 per cent of the oxidation product of castor oil, 2-15 per cent of neutral or acid salts of sulfo- fatty acids, 20-60 per cent of fatty acids, such as are obtained by the sulfurization of fatty acids followed by the splitting off of sulfuric acid, and 5-25 per cent of an aliphatic alcohol with more than 3 carbon atoms (also kerosene), may serve as a demulsifier in breaking water-in-oil emulsions.

Salts of estolides obtained from blown or dried oils or fish oils, together with organic amines, are also suitable demulsifiers. In the preparation of estolides, the blown oils are saponified by heating in the presence of a small amount of sulfuric acid, separating the acid and the glycerin, and further heating the product to about 115° for many hours, during which time an inert gas or air is introduced. Triethanolamine, monoethanolamine, amylamine, benzylamine, and piperidine are suitable amines. Likewise, blown oils, such as castor oil, dried oils, or fish oils with a low iodine number (below 20), may serve as demulsifiers. The oils may be freed from unsaturated bonds by treatment with non-acid agents, such as chlorine, bromine, or phosphorus, also by adding sulfur or bromine, and boiling in a reflux condenser. Estolides, obtained from blown oils, may be substituted for the latter. The estolides from blown or dried oils or fish oils may also be treated with ammonia under pressure (10 atmospheres) at about 180-200°. The products so obtained differ from ammonium salts of acids serving as a base because they also contain nitrogen in the amine-, imin-aldehyde ammonia-, or ketoammonia bond.⁵⁴⁹

A process for breaking petroleum emulsions has been proposed by Colbeth^{90a} in which the emulsion is treated with an unoxidized, polymer-

ized fatty oil, such as castor, rape, or corn oil. As a specific example for carrying out the demulsification may be cited the use of castor oil treated with about 1-10 per cent by weight of a boron compound, such as borax, boric acid, or boric anhydride, at a temperature of about 200° for approximately 30 minutes, or until foaming ceases. If boron trichloride or trifluoride is used, the oil must not be heated; bubbling the trichloride or trifluoride through the oil effects polymerization.

Polymerized, but not oxidized, fatty oils, such as castor oil, rape oil, etc., may be used as demulsifiers for breaking petroleum emulsions. In polymerizing, the oil is heated to about 195-425° for a short period of time so that splitting of the glycerin does not take place; it is then blown with air at about 250-375° for 4-10 hours, or polymerized with catalysts such as aluminum chloride, ferric chloride, zinc chloride, or especially with boron compounds such as boron chloride, boron fluoride, boric acid, or borax at about 200° for a short time (30 minutes), or until the initial foaming stops.^{29a}

Petroleum emulsions, such as bottom settlings, may be separated by subjecting them to the action of a blown fatty oil, i.e., blown castor oil which has been made to react with an esterifying agent. The esterification of the acid groups in blown oils may occur through compounds such as MeOH which replace hydroxyl or carboxyl groups. Likewise, phosphorus pentachloride, sulfuryl chloride, thionyl chloride, propanol, butanol, glycol, mannite, or sorbite may also be used. To effect separation of the emulsion, it is allowed to stand; an upper layer of oil and a lower layer of water and foreign matter are formed, the latter being withdrawn.^{29b}

Castor oil, rape oil, cottonseed oil, linseed oil, soybean oil, corn oil, chinawood oil, or fish oil, subjected to a stepwise oxidation at 160° for bleaching and then at 140° until large amounts of aldehyde acids are formed so that the oils become non-saponifiable, may be used as demulsifiers.

Distillation Products (Acid and Alkali Sludge, Cracked Residue, Paraffin Wax)

Kuczynski²⁸⁴ patented a method for the separation of emulsions involving the addition of small amounts of substances formed by the distillation of bitumen compounds, e.g., phenol-containing tars, tar ingredients boiling above 150°, such as phenols, cresols, xylenols, aniline, and their homologs which, at the same time, may serve to prevent the formation of stable emulsions. For example, 100 kg of crude-oil emulsion containing natural salt with about 25 per cent of a bitumen were allowed to stand with 5 kg of coal tar at room temperature for 24 hours; complete separation of water took place.

Edmed and Newington¹³⁵ separated oil from emulsions, such as residues from fuel oil storage tanks, by the addition of tar or creosote or their fractions, or of phenols or cresols or their homologs, using air or mechanical agitation and gravity stratification. The water drained off

was passed through coke breeze or other filtering material. The whole process is expedited by heating the substances.

Erlich¹⁴⁷ recommends the utilization of alkaline kerosene sludge in the demulsification of Grozny lubricating-type crude oil. Before distillation in a pipe still, the oil receives a preliminary treatment with 3-3.5° Bé sodium hydroxide and an admixture of about 10 per cent of alkaline kerosene sludge. The ceresin emulsions derived from the Grozny-Tuapse pipe line are readily decomposed by heating with steam in the presence of 5 per cent of sodium chloride.

Pester³⁷⁸ treats emulsions with 0.25 to 5.00 per cent of resin acid obtained by refining mineral oil with fuming or concentrated sulfuric acid. The mixture is heated to 77°.

According to Fisher and Reddish,¹⁵⁹ sodium salts of mineral oil sludge of sulfo- acids, alcohol, and a bituminous substance melting at 35-95° form a homogeneous reaction mass. When this is stirred with an emulsion and warmed, demulsification is effected.

Demulsifiers may be prepared from acid sludge obtained in the treatment of white oils. Acid sludge from the third to the seventh-eighth treatment of white oils with oleum is washed with small quantities of water to remove the sulfuric acid and neutralized with a solution of sodium hydroxide also added in portions and with steady agitation. To improve the demulsifier, any kind of petroleum product, such as kerosene, gas oil, etc., may be added at temperatures of 50-90°. The oil extracts the tars in a very thorough manner. The efficiency of this demulsifier is claimed to be the same as that of naphthenic acid, and provides a saving of about 10 per cent of the treated oil.³⁷³

The General Petroleum Corporation¹⁷⁸ separated acid sludge by hydrolysis. First, a stream of emulsion was allowed to flow through a mass of inert granular material to bring the dispersed particles into contact with it, and the diluted acid was drawn off. The acid sludge was then mixed with dilute sulfuric acid, the density of which is greater than that of the sludge. The Standard Oil Development Co.⁴⁹⁵ separated emulsions, consisting of hydrocarbons and water, by the addition of $\frac{1}{4}$ to $\frac{1}{5}$ per cent of acid sludge. Mineral and lubricating oils are also treated with fuming sulfuric acid or sulfur trioxide.

A reagent consisting of a layer of mineral oil sludge, aluminum sulfate and sodium hydroxide may be used in breaking petroleum oil emulsions.²⁷⁴

Another reagent⁵³² for breaking petroleum emulsions of the water-in-oil type consists of approximate molecular proportions of naphthalene, the middle distillate of pintsch gas-tar having a boiling point of 85-120° F, and a cycloölefin having not less than 7 and not more than 17 carbon atoms in the ring, treated with an excess of strong sulfuric acid, washed with water, and neutralized with strong ammonia.

The use of soaps for breaking emulsions apparently is not favorable. Acids are sometimes likely to cause considerable trouble. A sodium carbonate solution of 44° Bé or stronger is excellent for breaking an

emulsion. Another method ⁴²⁶ is the addition of sufficient sodium carbonate until the emulsion becomes alkaline, followed by heating with steam and blowing air through it until separation occurs. In breaking acid-treated emulsions, it has been suggested that the sodium carbonate necessary to neutralize each batch be determined by titration, using a sodium carbonate of the same strength as will be used in plant neutralization. The sample is shaken with a mixture of 50/50 benzene-alcohol prior to titration, thus breaking any acid emulsion which may have been formed.

Hendrey and Ebaugh ²²⁴ claim that emulsions of the water-in-oil type are resolved by maintaining them at a temperature of 180-200° F in the presence of a small quantity of aqueous alkali solution and still bottoms from the vacuum distillation of lubricating oils.

Roberts ⁵⁹⁹ breaks petroleum emulsions by treatment with a halogenated, hydroxy-aldo or keto derivative of a petroleum hydrocarbon. This reagent is obtained from Pennsylvania petroleum distillate (b.p. 250-325° C $d^{20}_4=0.8125$) (U. S. P. 1,681,237), and is a mixture containing less than 70 per cent of aldo-fatty acids and less than 30 per cent of aldehydes and unaltered hydrocarbons. The acids obtained on distillation are chlorinated.

Curtin ⁹⁹ breaks petroleum emulsions containing at least 5 per cent of asphaltic bodies by mixing them under pressure with low-temperature petroleum having a tar content of 0.5-4.0 per cent by volume.

A dehydrating method for petroleum emulsions has been patented by the Texas Company.⁵⁹⁹ The emulsions of crude oil or fuel oil are broken by treating them with 0.1-1.0 per cent of still bottoms from the vacuum distillation of oil. These still bottoms are neutralized with sodium hydroxide, if not already alkaline; and they contain undistilled heavy oil within the lubricating oil range and alkaline salts of naphthenic acids of a high molecular weight. The treatment takes place at 82-93°; it consists in circulating the hot emulsion through a pipe system into which the hot demulsifying agent is introduced on the suction side of the pump.

Petroleum emulsions of the water-in-oil type may be dehydrated by adding to them 0.1 per cent of the ammonium salt of oxidized paraffins and heating for 12 hours up to 70°. Oxidized paraffins are obtained by passing air at 150° through the paraffins, to which has been added one per cent of magnesium resinate; this results in the formation of up to 65 per cent of saponifiable substances.³⁹

For demulsification of petroleum emulsions, the use of a fraction consisting mainly of the acidic products from the oxidation of petroleum hydrocarbons at 155° in the presence of manganese oleate is claimed. The fraction containing ketonic compounds or the products of sulfonation thereof may also be employed.⁸

Separation of emulsified oils is effected by treatment with a spent sodium hydroxide solution, previously used in oil refining operations for washing hydrocarbon oil or oil refinery gases, and heating at 65°, or until stratification occurs. Likewise, a spent alkali solution derived from the neutralization of sour oils may be used.⁴⁰³

Mushkin³⁵⁶ suggested using a heated layer of water for demulsifying petroleum products. A crude-oil emulsion containing 30 per cent of water was broken in 5-6 days by heating a layer of water in the bottom of the storage tank to 65°. An oil with 0.3-0.8 per cent water content resulted. About 50 per cent of fuel was saved in comparison with the usual method. Baku crude-oil emulsions are completely broken after treatment with 4.0 per cent of cracked residues at 65-80° for 12-36 hours. The heating temperature depends on the initial boiling point of the crude oil and should not be higher than this temperature.²⁷⁷

A process for breaking emulsions from Kala crude oil, applied on a commercial scale, consists in treating the latter (containing up to 6.2 per cent water) with cracked residues at 65-80°. About 87 per cent of the water was separated in 12 hours and all of it in 24 hours, whereas at 40° up to 96 per cent of the water was separated after settling for 36 hours. On treatment with cracked residues, complete separation followed in 60 hours.⁴¹³

Robinson⁴³⁷ developed a dehydration process involving the addition of a hydrocarbon such as naphthalene, acenaphthene, phenanthrene, or paraffin wax, which also serve to resolve emulsions containing tar oil. Naphthalene, which is soluble in either the tar or the oil, has a melting point below 100°. Robinson states that a large proportion of the phase containing the tar-oil agglomerates, together with the hydrocarbon, forms a thick mass, and that most of the aqueous phase separates from this mass. Preferably, the hydrocarbon should be added to the emulsion and dissolved in it by heating until a uniform consistency is obtained. The resulting mixture is cooled rapidly by stirring to effect separation of the hydrocarbon in a finely divided, crystalline form. It has been claimed that this method is particularly suitable for resolving heterogeneous emulsions such as are found in tar and gas works, water-gas tar or other tars blended with emulsions containing creosote or similar oils.

To increase the production of oil is a problem in itself. In order to raise the production of declining wells, they are treated in succession with acid, oil, and alkali, which diffuse under pressure, forming concentric rings. These rings become smaller and smaller until a chemical reaction between acid and alkali takes place, heat and gases are set free, and the production of oil is increased.⁹²

De Groot (Tretolite Co.⁵⁴²) increased the productivity of petroleum wells by lubricating the drill with an emulsion of dilute acid in oil, using a mixture of hydrochloric acid and nitric acid in a ratio of 5:1 to 3:1 calculated with respect to the unchanged acids. For example, in the preparation of the emulsion, 400 gallons of oil and 100 gallons of dilute acid, containing at least 15 per cent of concentrated acid, are used. To remove cement seals in drill holes and thereby increase the production of oil, these are treated with acetic or propionic, butyric or formic acids (about 30 per cent), whereby the cement is decomposed after a few hours, the acid neutralized, and the cement sludge washed out from the drill holes.⁵¹⁰

The Gulf Research and Development Co. (Ayrre⁵⁰²) prevent access of water to drill holes by injecting carbon dioxide under pressure, which reacts with the lime and water present in the formation, forming soluble bicarbonate. The remainder of the carbon dioxide is released; thus the bicarbonate decomposes and clogs the pores of the formation. If the formation contains too little lime, a solution of calcium acid carbonate is added to the drill holes. When a formation contains too much chloride, an ammonia solution is pumped into the drill holes after the carbon dioxide has been released, in order to precipitate the soluble calcium salts.

Halliburton Oil Well Cementing Co. (Clason^{300a}) proposes acid treatment of oil wells having several oil-producing formations. After the lowest oil-bearing formation is treated with acid (hydrochloric) in the usual manner, a soap solution is pumped into the well; this likewise penetrates only to the lowest formation where it enters into reaction with calcium chloride solution (formed from calcareous rock and hydrochloric acid), forming a temporary insoluble compound and rendering the layer impervious to water. After the well is filled with calcium chloride solution up to the height of the next oil-bearing formation, this also is treated with acid. After the liquid has been removed from the well, the penetrating crude oil dissolves the soap so that the pores in the lowest formation are open again.

The Dow Chemical Co. (Grebe^{177a}) introduces a granular, electrically conducting substance, such as coke, into which is inserted an electrically conducting tube of copper connected by an insulated cable with the negative pole as a source of direct current. The positive pole of the source of current is grounded. Finally, a heavy metal salt solution which serves as an electrolyte is introduced into the well under pressure, and the metal is precipitated in the water-bearing stratum by electrolysis. The density of the current must be 150-1500 amperes per square meter of the formation in order to make it impervious to water, and the voltage is 25-200. Suitable electrolytes may consist of a mixture of 350 g of $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{O}$, 0.25 g of H_2SO_4 , and 0.5 g of glue per liter, or 200 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 50 g of H_2SO_4 per liter.

Tretolite Co.³⁰⁰ describes a process for breaking water-in-oil emulsions in which the solutions in a well are subjected, before emerging from the well head, to the action of a demulsifier, such as calcium carbonate, magnesium carbonate, barium sulfate, and others, together with the sodium salt of monopropylated naphthalene sulfonic acid.

As a preventive measure for emulsion formation in oil wells, making the water-bearing strata impervious has been suggested. For this purpose, a soap solution which penetrates into both the petroleum and water-bearing strata is introduced into the well. Due to the presence of soluble inorganic salts, such as sodium chloride, calcium chloride and magnesium chloride, a precipitate is formed in the water-bearing strata by the reaction between these salts and the soap solution; this precipitate clogs the pores of this formation, but does not affect the petroleum-bearing formation.⁴⁰⁷

A water-in-oil emulsion containing two distinct phases, one an acid solution, such as hydrochloric acid, the other a fluoride solution, such as calcium fluoride, is introduced into a well without affecting its metal parts; subsequently the phases react to form hydrogen fluoride on demulsification of the emulsion. This method serves to increase the productivity of oil, gas, water, or brine.⁵⁴¹

The underground treatment of emulsified petroleum is carried out by feeding a flowing stream of water into the well and injecting into the stream a water-insoluble treating agent of the modified fatty acid type, such as sulfonated castor oil or the like, conveyed in the form of unemulsified macroscopic droplets to the producing zone of the well, where it serves to effect demulsification.⁵⁰⁷

Sometimes the production of oil and gas wells drops or stops entirely after a short production period. This is due to the fact that paraffin wax, asphalt-containing substances, inorganic salts, and similar substances are precipitated in the form of films or coatings on the channels or pores of the strata. These are removed by forcing through the layer a 0.5-5.0 per cent mixture of oil and water containing two wetting agents, one, *e.g.*, petroleum sulfonate or an ammonium salt of sulfonated oleic acid, the carboxyl group of which is esterified by methanol, ethanol, propanol, or butanol, dissolved in crude oil, gasoline, etc.; the other, *e.g.*, ammonium amylamine-, benzylamine-, butylamine, or the toluidin salt of propyl- or butyl- β -naphthalene sulfonic acid in a 0.5-5.0 per cent aqueous solution, followed by treatment with hydrogen chloride or hydrogen fluoride.

It has also been proposed to force through the formation an acid-in-oil emulsion which demulsifies only after a long time. This emulsion is prepared according to de Groote (U. S. P. 1,922,154, Aug. 15, 1933) using, however, one and one-half to two times the amount of emulsifier required; the emulsion is soon broken by the action of capillary forces. After 2-12 hours, a "dormant" demulsifier is added, such as phenol, cresol, naphthol, tar acid fractions, aliphatic acids of acetic to lauric acid, hydrochloride, solutions of starch, gelatin, casein, resins, phenol-, cresol-, xylene-, naphthalene-, ethylnaphthalene-, tetralin-, hexanolsulfonic acid, or cresol-, toluene disulfonic acid. The process for increasing the output of oil wells consists in introduc-

ing into the well a relatively stable emulsion of an aqueous hydrochloric acid solution of about 15 per cent strength and adding one per cent of nitric acid emulsified in an oil vehicle in such a manner that the acid-in-oil emulsion passes the metal parts of the well without having any deleterious effect on them, and thereafter reacts with the capillary, oil-producing, calcareous strata. The emulsion to be applied for treatment may be prepared by using, in addition to the above demulsifier, 0.1-0.5 per cent of a foaming agent, such as pine oil, mixed with 15 per cent of hydrochloric acid. By introducing air, natural gas, or carbon dioxide, the mixture is converted into a foaming mass with possible small bubbles, to which is added, with stirring of the crude oil, the naturally occurring emulsifier.⁶⁴⁶

The production of oil wells may be increased by removing precipitates of organic compounds from the petroleum-bearing formation by means of a suitable liquid, such as a dilute aqueous solution of a capillary-active substance which does not affect the formation. For example, a sulfonic acid obtained from the refining of mineral oil with sulfuric acid, or the sulfonation product of fatty oils, unsaturated hydrocarbons, alcohols, naphthenic acids, oxidized paraffins, or the salts of these substances, is such a liquid. According to Dutch Patent No. 43,894, mineral oils from oil-containing sands should be treated with aqueous solutions of capillary-active substances. Acid esters obtained by the action of polybasic inorganic acids, especially sulfuric acid, upon saturated or unsaturated alcohols, unsaturated aliphatic hydrocarbons, or the salts of these substances, are recommended.⁶⁴⁶

Freezing and Diluting Methods

Water may be separated from oil present in an oil-in-water emulsion by freezing. When water changes into ice, it expands and this expansion breaks the oil envelope. This oil envelope is not rigid, but more or less elastic. Thus several alternate thawings and freezings are necessary to effect complete separation. If the temperature is lowered sufficiently to convert the oil into a solid, the rupture of the envelope is complete, and separation of the oil from the water takes place on thawing. The solidifying temperature is frequently very low, but can easily be attained by the use of liquid air. This method of dehydration does not find application on a large scale. Very few patents are concerned with freezing-out processes.

Freezing is an excellent method, but it has doubtful value in the refinery. The breaking of an emulsion by freezing may be explained by the withdrawal, as the result of the formation of ice, of free and/or combined water from the films between droplets which are in contact, or by an increase in the concentration of the solute, followed by true contact between adjacent films of the emulsifier, with loss of the orienting influence of water. The emulsifier in the film diffuses from these regions and the film area decreases, with the result that the droplets coalesce as soon as thawing of the ice permits them to change shape. This explanation is given for the phenomenon of breaking emulsions by freezing by Rochow and Mason,⁴⁴⁰ who observed microscopically emulsions prepared from carbon tetrachloride, benzene ($d=1$) and water, with and without an emulsifier (sodium or ammonium ethyl oleate), when subjected to freezing and subsequent thawing. In studying the breaking of emulsions by freezing, Rochow and Mason ⁴⁴⁰ state that microscopic observations verify the existence of a plastic membrane surrounding each globule, and consider that the destruction of the membrane, rather than mere freezing of the continuous phase, is essential to coalescence of the globules.

The usual demulsifying methods, such as thermal treating, centrifuging, etc., are not suitable for separating oil from alkali naphthene-containing residues from mineral-oil refining. However, good results were obtained²⁵³ by freezing at -15° to -21° the residual water from machine oil refining which contained about 5.5 per cent of naphthenic acids and over 92 per cent of mineral oil in the organic phase, and thawing by heating to $50-60^{\circ}$.

Repeated freezing, with the addition of sulfonic acids or alkali residues from the refining of illuminating oil as demulsifiers, is recommended. Reuss⁴²⁷ described a method for dehydrating tars. Tars containing water are permitted to freeze and then to melt. Tar and water are separated sharply. The same principle was applied by the experimenter to the dehydration of other emulsions.

Egloff and Benner¹⁸⁷ dehydrated emulsified oil in a still by subjecting it to a temperature below the freezing point of water and passing a refrigerating medium through a coil within the still. This causes the water and oil to stratify, and the separated water is withdrawn from the still. Heated gas is then passed through the coil within the still, the temperature of the oil being raised to the cracking point and the cracking effected under superatmospheric pressure.

Dilution may react unfavorably if it increases stability and resists agglomeration. A gelatinous emulsion that slowly yields some of its oil as a continuous phase by agglomeration and subsidence does not produce this effect after dilution. Whether or not dilution causes a separation of oil from an emulsion depends on the influence of dilution upon other variables of the emulsion system, such as the concentration of the emulsifier, alkali, and protective colloid in the emulsion.

Desalting Process

It is known that emulsoids can be precipitated by means of electrolytes and that a much greater quantity of the latter is required than in the case of suspensoids. This effect of electrolytes—"salting-out"—differs from flocculation. Ammonium sulfate, magnesium sulfate and sodium sulfate are considered most suitable for salting out emulsoids. These salts are very soluble and may be used in comparatively high concentrations. Solubility of the salt used for the purpose of salting out is not the only determining factor, since magnesium sulfate, which is less soluble than magnesium chloride, may be used to salt out agar-agar, whereas the chloride is not suitable even in high concentration. Salting out is naturally related to the nature of the cation (lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, barium) and of the anion (sulfate, chloride, bromide, nitrate, iodide, sulfo cyanide).

In the lyotropic series, the influence exerted by the ions is apparently such that those at one end favor association, while those at the other end promote dissociation. In the lyotropic series, when the electrolytes are used in equal molecular concentration, the precipitation power

decreases from left to right. According to Kruyt,²⁸¹ salting out consists in a discharge followed by dehydration. Salting out is obviously related to the ability of ions to take up water, and the electrolytes acting on the emulsoids withdraw water from the sol. However, the removal of water is brought about in the order of the lyotropic series, the small initial amount of the added electrolyte performing the capillary electrical task.

Certain crude oils as recovered from wells contain a large amount of salts or brines which, if not removed before refining, clog and corrode the refinery equipment. The refineries of continental Europe use hygroscopic salts for the desiccation of petroleum, *i.e.*, calcium chloride and magnesium chloride in the fused form in solid blocks of about 8-10 hundredweight. In preparing the brine, the salts are dissolved, preferably in ordinary spring water. Usually the circulating brine is controlled by an aerometer to maintain the right density, which is kept higher than theoretically necessary in order to compensate for unforeseen losses in the piping system, *etc.*⁵⁰³

Oils are desalted and demulsified by treatment in the continuous phase with a mixture of sodium hydroxide and a soluble alkali acetate with ethyl alcohol and glycerin. An after-treatment with an acid carbonate solution may be desirable. The preferred composition of the reagent is sodium hydroxide 25 per cent, sodium acetate 10 per cent, ethyl alcohol 20 per cent, glycerin 10 per cent, and water up to 35-45 per cent.

Even a small proportion of salt in an oil, as shown by the following approximate calculation, may be significant to a refiner. A crude oil containing one-half per cent of oil-field brine of average salinity (*sp. gr.* about 1.12) may contain as much as one-third of a pound of salt per barrel of oil, but all this salt is in solution in a small percentage of water. A refinery handling about 6000 barrels per day of such crude oil would take about one ton of salt into the system every 24 hours.

Usually brines contain an appreciable percentage of calcium and magnesium chlorides. These salts are hydrolyzed by the water in the crude oil during distillation, thereby liberating into the refinery system highly corrosive hydrochloric acid. When hydrogen sulfide in addition to hydrochloric acid is present in the fractionating equipment, the corrosion becomes exceptionally severe. Corrosion may be accounted for by the reaction between iron sulfide and hydrochloric acid, resulting in the formation of ferrous chloride, which in turn is oxidized to ferric oxide by moisture or other sources of oxygen. Corrosion is limited only by the amount of oxygen available, either as water vapor or air, or in the constituents of the oil. Desalting eliminates corrosion, reduces costs of neutralization, and eliminates the necessity of using expensive acid-resisting alloy metals. If the oil is treated as it is lifted, the emulsion can be reduced fairly easily. In some fields in Kansas there are emulsions which are particularly hard to break, especially when the oil has been standing in stock tanks for a considerable time. The Skelly Oil Company has designed an efficient treating plant which reduces the free water in

the oil to less than 1/10 of one per cent, and the saline content from 16,400 grains per barrel to about 8 grains per barrel. This plant consists of three vertical columns, each of which includes an oil and a gas separator in the top section. The lower part of the column contains a predetermined amount of water through which the oil must pass. During the passage of the oil the temperature is raised to the most efficient treating point. Special chemicals are used as treating compounds. The treater is operated at a temperature and rate suitable for the particular emulsion.²

Herschman²³⁶ patented the desalting of crude oils and the breaking of crude oil emulsions by treating them with a mixture of bleaching powder and at least one of the following compounds: sodium perborate or peroxide or hydrogen peroxide. In another patent, Herschman²³⁷ proposes a method for desalting and demulsifying oils which involves mixing the oils in continuous phase with a desalting and demulsifying reagent consisting of caustic soda approximately 25 per cent, sodium acetate about 10 per cent, alcohol about 20 per cent, glycerin about 10 per cent and water about 35-45 per cent. Desalting has also been successful when applied to Michigan crude petroleum. The major portion of the salt content is removed by treating with about one per cent of an alkaline solution of sodium acetate and adding to the partially desalted crude oil a bicarbonate solution at about 130° F under pressure.

South Electra Texas crude contains on an average about two per cent of salt water, which is detrimental to the life of the still bottom, causing it to blister. The deposits of sand and salt also accelerate the formation of coke. The Dale Oil and Refining Company has installed a flash tower, which acts as a sand and salt accumulation drum, and has placed it in the line between an economizer and the first shell still to receive the oil at an average temperature of 290° F. Up to the flash tower the oil is carried at 45 pounds pressure, maintaining practically all the water as liquid carrying the salt in solution. The flash tower removes the water and a part of the light vapors in the oil, at the same time serving as a drum which receives the sand and salt released into it. There is a by-pass line around the tower allowing it to be cut out of service when the accumulation has been built high in the base of the tower. It is claimed that as much as 15 tons of salt and sand can be removed from the primary flash tower in one week, depending upon the condition of the charging stock.

A method frequently used in reducing crude to a salt-free state is to heat the charge by passing it through various types of heat exchangers. Heating the charge to higher temperatures by placing steam coils in the crude settling tanks has been suggested. Many plants have clover-leaf coils inserted in the fractionating column, usually in the top section, as well as in the kerosene section. This type of processing secures heating the charge and controlling the tower temperature. The Leonard Refineries, Inc. at Alma, Michigan*, have built a plant to reduce the volume

*The Leonard Refineries now use electric desalters at Alma, Michigan.



FIG. 26a. Heat Exchangers, Leonard Refineries, Inc., at Alma, Michigan, to Heat Crude Charge Entering Salt Settling Drum.

of salt of a crude carrying varying quantities of salt averaging from about 220 to about eight pounds per thousand barrels of crude charged to the plant. The crude is passed through several heat exchangers in an amount small enough to prevent deposits from forming in the furnace tubes, and corrosion of the condensing equipment on side streams removed from the fractionating column.

The crude passes from the top clover-leaf coil to the one placed in the top midsection to adsorb heat from the tower temperature (150° F). While it is flowing through piping to the base of the tower where a bank of exchangers is installed, the temperature is raised to about 210° F. Three rows of tubes in the convection section of the furnace preheat the

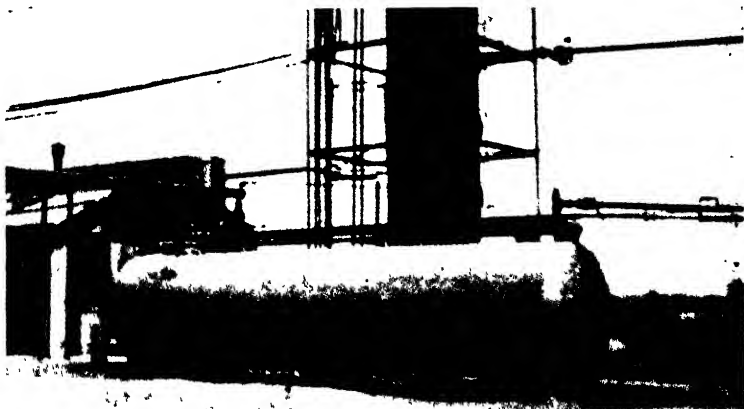


FIG. 26b. Tank Used at Leonard Refineries, Inc., at Alma, Michigan, to Remove Salt from Crude Charge.

oil to about 250° F before it flows to the salt settling drum. Pressure maintained upon the charge while in the drum averages between 50 and 60 pounds. From the drum the charge enters the furnace the second time (*Refiner and Natural Gasoline Manufacturer*, 15, 582, Dec., 1936).

The oil from wells in the Crystal Field, central Michigan, has an exceptionally high gravity, running from 44-48° A.P.I. The temperature required for efficient separation if wooden tanks are used is 135-150° F. In 1936 the Pure Oil Company installed a wooden "gun-barrel" tank and a double Dutch oven heater in several Michigan fields for separating salt water from oil. In order to obtain the proper heating temperature, one-half of the fuel previously used in the Michigan fields exclusively for steel tankage was required. All the salt water is disposed of either by pumping or forcing it under separator pressure into the underground stratum of a glacial drift.



FIG. 27. Petroleum Rectifying Co.'s Desalting Unit in Refinery of Lion Oil Refining Co. at El Dorado, Arkansas.

An electrical process for removing harmful and corrosive salts from pipe-line oil, so as to reduce corrosion in refinery equipment and improve the quality of refined products, has been proposed by Eddy (*Petroleum Rectifying Co.*³⁸⁷).

The Petreco electric desalting plant is an integral part of the refinery system. Four thousand five hundred barrels of crude oil may be desalted per day, about 95 per cent of the salt being removed. In the refinery of the Lion Oil Refining Co.³⁰⁴ (Fig. 27) a Petreco Electromatic desalting plant has been installed by the Petroleum Rectifying Co. It consists of a desalting unit for processing a heavy Arkansas crude oil containing as much as 180 g of salt per barrel, an amount sufficient not only to cause corrosion of the equipment, but to deposit crude salt in the exchangers and other parts of the installation. This crude is difficult to break because the emulsified brine is surrounded with a tough film of asphaltic oil. Because of the large amount of oil processed daily (4000 barrels), two units, each containing two treating containers and operated parallel to

the other, were installed. Each pair of containers (10 by 12 ft), of standard A.P.I construction, is equipped with heat exchangers, weight-loaded valve, flowmeter, orifices and back-pressure regulators. The oil containing the emulsified brine is pumped to the units from the plant working tanks through the desalting heat exchangers. The desalted oil flows through the heat exchangers counter-current to the fresh charge, to a point in the system where hot water is injected into the stream.

The back-pressure regulator is located on the dry oil discharge line from the units and serves to maintain the desired pressure in the treaters. The water is delivered from the boiler feed pumps with a volume of about 20 per cent of the oil at a temperature of 170° F. When the oil first contacts the water it has a temperature of about 140° F. The oil and water form an emulsion which is directed into the treating units for the removal of water. A predetermined level of water is maintained in each container and the emulsion is introduced above that point; the minute droplets of water coming into contact with the electrical field coalesce into larger droplets which separate readily from the oil; water falls to the bottom of the tank and the oil rises to the outlet. The saline content of the oil has been reduced to as low as three grams per barrel on the outlet of the treating units. The cost is not excessive. The Petreco desalting process is considered to be a commercially feasible method by which the salt content of large volumes of oil can be reduced. Other salt removal processes leave a relatively high percentage of the salt in the oil.

The Lion Oil Refining Co. desalt their corrosive crude in an electrical unit, reducing the salt content from 100 to 4 g per barrel. Tests indicate that corrosion is reduced to a minimum because the evolution of hydrochloric acid is decreased from 63.85 to 0.54 lbs per 1000 barrels of crude at 650° F. The salt-bearing crude is emulsified with 5-20 per cent of fresh water and then passed to a low-pressure (25 lbs) dehydrator tank (180 barrels capacity) equipped with electrodes. The electric field imposed has an average gradient of 10,000 volts per inch. Operating temperatures may vary from 130-200° F. Salt water is thrown out of the oil and removed. The process is continuous and the average throughput per day per unit is 1500 barrels.⁷

The Barnsdall Refining Co. (Wichita, Kansas) processes crude collected from various fields with an average gravity of 39° A.P.I. In addition to the Dubbs cracking unit, the refinery also has a desalting unit. The crude oil charged to the pipe stills in this plant contains a varying quantity of salts, principally sodium chloride.* The total volume of salts varies from 10-118 pounds per 1000 barrels of crude. When running crude of this type, mechanical stoppage of tubes in the pipe still and corrosion throughout the plant may be anticipated. To eliminate salt coming in with the crude, three units of Petroleum Rectifying Co. apparatus were installed. The capacity of the three units is 5500 barrels

* Analysis of certain crude coming into the plant showed: calcium chloride 28 lbs, magnesium chloride 3 lbs, ferric chloride 11 lbs, and sodium chloride 66 lbs.

of crude daily. The fluid temperature varies from 125 to 150° F. A mixture of three parts of crude and one part of hot water is admitted through an emulsifying valve into electric treaters where water is separated from the oil. Within the units is placed an electric field with a potential of 33,000 volts. Two units of concentric rings are within the containers, each connected to a transformer mounted upon the top of the container through an entrance bushing. The emulsified oil is introduced into the container so that it is distributed into the electric field. Allinson⁶ describes electric desalting of crude oil by subjecting the emulsion to a strong electric field.

Egloff, Nelson, Maxutov and Wirth¹⁴¹ studied the effect of temperature and pressure on desalting of a Mid-Continent topped crude. They found that the salt content was decreased by increasing the temperature or the percentage of water added. Optimum conditions established were 10 per cent of water and 400° F. The pressure should be sufficient to keep the water in liquid form (about 300 lbs per sq in at 400° F). Agitation sufficient to bring about an intimate contact between water and salt particles was recommended. The amount of salt water withdrawn increases with increase in settling time, while the concentration of salt in it reaches a maximum and then falls off. It has been thought that the water globules carrying the higher salt content coalesce more rapidly than those of lower salt content. At low settling temperatures, the percentage of water in the treated oil decreases more rapidly than the percentage of salt because the unaffected films of asphaltic and paraffinic substances stabilize the salt particles. At higher temperatures, the reverse is true because such films are absent.

Filtration as a Means of Dehydrating Oils and Emulsions

Among physical methods used for dehydration, those involving filtration and ultrafiltration assist and supplement other general methods used in the resolution of emulsions. Thus the filtration method has possibilities, especially when combined with other processes. The adsorption method is usually applicable on a small scale, or at a time when expense and material as well as the slowness of the dehydration process may be disregarded.

Between the adsorbed substance and the adsorbent there exist certain physical and chemical forces of attraction. The former exert action upon the whole surface, and this action is unlimited and quite strong. The latter are forces of "affinity," and are therefore specific with a limited sphere of action regulated by atomic distances. In the case of emulsions, the cause of adhesion of oil to an adsorbent like carbon is an attraction having a larger sphere of action (a molecular attraction) than that corresponding to the chemical attraction, but weaker in intensity than that of the physical nature. A stick of pure, electrolyte-free carbon placed in a Santa Maria crude-oil emulsion shows a decided attraction for the oil in a diluted water-in-oil emulsion. Around the carbon stick

a kind of gelatinization is observed (S. Berkman). Sludging of emulsions or formation of a pseudo-gel so often found in crude oils on standing are based on the approaching and reciprocal binding of hydrated particles exerted by forces of molecular attraction between the hydrated particles. In general, gelatinization is influenced by certain factors, such as increase in temperature, change in concentration, presence of by-products, etc.

In emulsions, strong forces of attraction toward the oil are not always exerted by different adsorbents; usually the emulsion is passed through an adsorbent body consisting of capillaries, either by means of a pump, an elevated tank, or other suitable pressure-developing devices on the inlet side, or by a vacuum pump, syphon, or other devices for obtaining, on the outlet side, pressures lower than atmospheric. An increase in the temperature of an emulsion subjected to treatment before forcing it under pressure through the capillaries minimizes the tendency to re-emulsification. Actually, the method of filtering emulsions is not comparable to a filtering operation. In a filtration process the purpose is to remove a solid substance from a liquid so that one substance passes on, leaving the other behind, deposited on the filter. In the method applied for the dehydration of emulsions the primary object is to separate two liquid phases, both of them passing together through the porous or capillary medium, which acts neither as a filter nor as a strainer, but as a device for breaking and coalescing the globular particles of an emulsion.

According to Dyer and Heise,¹²⁴ particles in highly concentrated emulsions assume a polyhedral shape. When these polyhedral particles are forced into a capillary passage they are subjected to the action of unsymmetrical forces by friction, impact, capillary action or other causes, accompanied by destruction of their envelopes. The result is the same as in the case of freely suspended spherical droplets. Oil and water flow through small openings with different degrees of freedom, depending upon whether the effect is caused by capillary action, frictional resistance due to the viscosity of the components themselves, or other reasons. It is further assumed that, as a consequence of forcing a mixture of oil and water through very small openings, the two components move at different velocities, so that certain portions of the stream become rich in water and others rich in oil. This tendency facilitates the separation of the two liquids after the rupture of the surrounding envelopes takes place. This kind of filtration requires a multiplicity of capillary passages in the capillary medium. Therefore, a closely woven cloth, or any other kind of material of a porous character such as a mass of finely divided mineral matter, may serve satisfactorily as a body having openings of a capillary character. Regarding the relationship between the chemical composition of the material and its adsorbent abilities, no general statement has been made. Substances giving the same analytical figures often behave very differently, and those of dissimilar chemical composition sometimes act as effectively as demulsifying agents. The essential feature of all effective adsorption agents lies in the characteristics of

their surface. The physical conditions under which the adsorbing surface exercises its specific action, of course, should not be overlooked.

Gilpin and Schneeberger,¹⁸¹ on passing California crude oil through fuller's earth, found little fractionating effect at 20°, but they obtained satisfactory results at 70°. Dunstan¹²⁰ made a peculiar observation, namely, that cold bauxite which has been ignited and cooled in a vacuum desiccator loses its power of adsorbing sulfur derivatives from kerosene. When freshly heated up to 200°, it regains its activity. The degree of fineness of the adsorbent is important. He proved that the activity is approximately proportional to the mesh size:

Bauxite Mesh	Activity
40/60	1.0
60/80	1.7

Hatschek²¹⁷ proposed filtering oil-in-water emulsions through calcium carbonate to remove oil globules from water. The oil is retained and water passes through not because of the size of the pores, but because calcium carbonate is more readily wetted by water than by oil. Hatschek also filtered emulsions of the reverse type, like crude petroleum, using a medium more readily wetted by oil than by water, such as pulverized vulcanized rubber and iron sulfide, which permit the oil to pass through, retaining the water. It has been found that this method is not readily adapted to crude petroleum emulsions, for the globules retained do not coalesce except by contact; simple subsidence was found to work even better. The Cottrell "wetted septum" is a device used in an electric dehydrator for dehydration of crude petroleum emulsions and involves a principle contrary to that of Hatschek's filter. Cottrell⁹⁵ used a cellular medium (canvas) which was more readily wetted by water than by oil. In this case the continuous oil phase passed through because of the large size of the pores. The dispersed water also passed through but, due to the contact with the canvas, a certain amount of coalescence occurred. The only objection to the use of this material is that the larger globules coalesce while the smaller globules form viscous clumps which soon close the pores of the canvas; in a carbonate filter, in some cases, a continuous impervious layer forms, resulting in the appearance of cracks in the device.

Stein,⁴⁹⁹ discussing the filtration action of filter cloth with respect to emulsions, pointed out that stable emulsions are difficult to filter through fine-mesh tissues, whereas coarsely dispersed emulsions disintegrate readily by filtration. Garrison and van Loenen¹⁷² break petroleum emulsions by passing them through a porous mass of comminuted aluminum oxide so that the dispersed phase of the emulsion is agglomerated. Welsch⁶²⁹ breaks emulsions or oils containing wash waters by first passing them through a tower filled with substances having an oily surface and then washing with a light oil. In another patent Welsch,⁶³⁰ in order to separate oil from the emulsion, leads it first through a layer

of pumice, the oil droplets agglomerating and rising upward through narrow channels. Light oil serves to extract the last traces of oil from the water.

Eddy¹³¹ dehydrated petroleum emulsions by forcing the emulsion and a gas, such as natural gas, through a filtering material, *e.g.*, broken glass or iron filings, under pressure to alter the surface tension of the emulsion, and then subjected it to the action of a high-potential electric field. Manley and Knoss³²⁰ stated that a mixture of a filter aid, *e.g.*, fuller's earth or clay and the emulsion may be dehydrated by heating to 160-200° F and subjecting to a thickening operation. A partial separation of the emulsion is effected and the concentrated suspension is filtered to separate the filter aid from the liquid. The filter aid is re-used.

Joel²⁵⁸ claims that oil-in-water emulsions can be separated when wood pulp is mixed with dry oil of the same kind as that present in the emulsion. The mixture is permitted to flow into the filter apparatus under low pressure and in a rapid stream, a layer of wood pulp being formed on the filter of the apparatus and the emulsion forced through it. Dittersdorf¹¹³ breaks oil or tar emulsions in water by mixing them with sharp-edged particles, such as sand and fragments of glass. The mixing may also be effected in a warm filter chamber filled with other sharp-edged substances. Trumble⁶⁰⁷ passes oil-water emulsions through porous diaphragms of progressively increasing area in order to increase progressively the time of separation. Dyer and Heise¹²⁴ conducted emulsified oils through infusorial earth under pressure. McKenzie³³³ filtered emulsions through Celite, using a very fine infusorial earth in the form of a filter cake in the filter press. When California crude oil is filtered, such a filter press, with a filtration surface of about 600 square feet, may deliver on an average of 1500 gallons of oil. Gurwitsch²⁰⁹ indicates the disadvantage of using quartz, which is wetted by water, and pyrite, which is wetted by oil, for dehydration purposes because their surface becomes saturated by either water or oil, and the unchanged emulsion passes through. Conway⁹³ forces the crude oil through a series of small holes in the bottom of a large container containing hot water. Fleeger and Osborn^{100a} succeeded in effecting dehydration by conducting the emulsion under pressure through a series of specially constructed filters. Shaw and Beale⁴⁰⁸ patented a filtration apparatus for separating oil from water.

Insofar as the efficiency of a filtering method is based not on the size of the pores but merely on the contact of a single layer of canvas, the latter must be replaced by a thick bed of coarse, granular material. A column of granulated, vulcanized, cellular filter material, which retains its physical form when soaked in water, has been tried. The disadvantage of the non-porous vulcanized fiber is that the contact surface is not sufficiently large in comparison with that of other adsorbents, such as fuller's earth. The method is, therefore, particularly suitable for emulsions which do not contain foreign matter. For emulsions containing foreign matter, Hatschek proposed the ultrafiltration process, namely,

the passage of a liquid through a medium whose pores are small enough to retain suspended colloidal particles.

Hatschek²¹⁷ proposed the idea that membranes used for the separation of colloids are also suitable for ultrafiltration of oil-in-water emulsions. By using 5.0 per cent collodion filters Hatschek was able to filter emulsions, applying 4 atmospheres of pressure; a temperature of about 50° appears to be most favorable. Bechold⁴¹ indicates the size of pores in ultrafilters used for this purpose. Two different methods for the determination of sizes give the following values: 21 or 50-74 $\mu\mu$; therefore it is natural that oil particles of a diameter six to twenty times these sizes should be completely retained by this kind of filtration.

The adsorptive action of many substances has found practical application. Fuller's earth acts as a dialyzing septum permitting paraffins and saturated hydrocarbons to pass through freely, and adsorbing bitumens, aromatic hydrocarbons, sulfur and nitrogeneous compounds; the surface is said to be the determining factor.¹⁸¹ Similar viewpoints on this subject have been expressed by Gurwitsch,²⁰⁵ who ascribes the filtering action not to capillary attraction, but to a definite surface which has been exposed to adsorption. He proved that Floridin adsorbed solid paraffin from a solution containing petroleum spirit and benzene, but not from a lubricating oil. An interesting method for dehydration by adsorption is given by Rütgerswerke A.-G.⁴⁴⁷ This method is based partially on the formation of a reverse type of an emulsion and partially on adsorption, the latter taking place by the addition of brown coal ash, coal ash, blood charcoal, wood charcoal, bone ash, bog iron ore, iron oxide, clay saturated with lime, kieselguhr, slate, burned kaolin and barium sulfate. It is said that not all finely divided substances cause resolution of an emulsion, but rather those which act as weak alkalies, such as coal ash. In the dehydration of tar, Rütgerswerke succeeded in decreasing the percentage of the water content to a considerable extent. The water content of 1000 kg of crude material containing 75 per cent of water was reduced to 4 per cent by the addition of 200 kg of coal ash.

Cottrell^{384a} described a method of electric filtration of materials encountered in dehydrating petroleum emulsions. The mixture of a liquid, such as oil, and suspended material is treated so that a stream of the material moves in a given direction; an electric field is set up to move the suspended material in the opposite direction; by this means the latter velocity is greater than that of the composite stream and the suspended material is collected.

Electric Dehydration

During the past thirty years various processes for applying alternating current have proved to be quite successful in the dehydration of crude petroleum. Many theories have been offered as an explanation for the electrical precipitation of water.

When emulsions are subjected to the action of an electric field, its

action depends upon whether the oil side of the interfaces of the dispersed aqueous particles is stabilized chiefly by ions or chiefly by polar molecules, for adsorbed ions will respond directly and immediately to the applied field and will be set in motion at velocities and in directions dependent upon the relative strengths and distribution of the ionic and applied electric fields. Polar molecules, on the other hand, will not respond to the action of the applied electric field other than to orient slightly in the direction of the lines of force of the external field.

Ionic adsorption is essentially a dynamic and reversible phenomenon. As the interface ages, more and more polar molecules adsorb at the interface, displacing some of the ions formerly there. Here they persist tenaciously and more or less irreversibly because, unlike the ions, they are electrically neutral. The slowly increasing concentration of polar molecules at the interface results in a slowly decreasing net external electric charge, which will be reflected in a slowly decreasing cataphoretic mobility.

With regard to the water-in-oil emulsion type, one conventional method of separating the phases is to subject the emulsion to the action of a high-potential electric field, usually of alternating character. In such a field the dispersed globules are coalesced into droplets of sufficient size to gravitate from the oil. However, the viscosity of the oil forming the continuous phase may retard this coalescence. The emulsion globules must therefore be suspended in a less viscous medium.

In the oil-in-water type of emulsion, the external phase may be formed of a body of conducting liquid, such as water. Electrical treatment of such an emulsion may be impossible in view of the fact that the water phase bridges the electrodes and in effect short circuits the electrodes sufficiently to prevent a building up of the potential difference requisite to electrical treatment. The action of an electric field is readily seen in a micro-moving picture film. The resolution of an emulsion also can be seen under a microscope.

Laird and Raney²⁹² patented a process for breaking emulsions by passing them upward between electrodes brought intermittently to a high potential difference, causing the conducting particles to coalesce in chains. When the potential is removed, these chains break up into globules of free water. Muth³⁵⁷ has observed the formation of chains when an emulsion was subjected to an electric field.

Kuczynski²⁹⁰ studied the behavior of emulsions in an alternating electric field and found that the droplets became deformed and formed chains parallel to the lines of force of the electric field. In water-in-oil emulsions, coagulation occurs when the globules of a chain make contact. In consequence, the chains conduct the current and show characteristic mutual repulsion. In emulsions of the oil-in-water type, the chains do not coagulate. Kuczynski observed also that two or three droplets may form chains at an equal distance to the lines of force of the electric field, these chains lasting for a certain time, or until convection currents destroy them. A high-tension field produces longer and more stable

chains; in this case the convection current is unable to break them. Sudden discontinuance of the current causes the emulsion to spread and to reach a homogeneous concentration. Kuczynski calls the chains conducting the current "conducting chains" or "detective chains." Chain formation, while occurring under certain conditions of static observations, does not usually occur in practice when the fluid is in motion; it is not a factor aiding electrical dehydration but, on the contrary, hinders the process, and is avoided whenever possible.

It has been proved also by Kuczynski²⁸⁰ that the emulsion has various dielectric constants depending on the nature of the disperse phase. The electric energy applied to the emulsion is expended not only in polarizing the dielectric, but also for mechanical work, *i.e.*, the deformation of droplets and changes in concentration. Kuczynski proved mathematically that if the emulsion droplets were small in comparison with the condenser, then the dielectric constant was independent of the size of the suspended particles, being a function of their total volume.

When an emulsion is subjected to the action of a non-uniform electric field, local changes in concentration occur, because of the movement of water particles from zones of low field intensity to zones of high field intensity, thereby decreasing the total internal energy of the system and tending to make the electric field more uniform. Coagulation phenomena occurring in an emulsion placed in the field of an alternating potential were photographed by W. O. and H. C. Eddy.¹²⁵ In these photographs the droplets of an emulsion formed radial chains up to a certain time. This, in all probability, was because a radial field was employed. The investigators assumed that these arcs were pictures of lines of forces occurring in the electric field, and that especially favorable conditions for coagulation may be afforded by subjecting the emulsion to a non-uniform electric field, although complete coagulation also occurs in uniform fields. Pawlikowski's³⁷⁷ experiments regarding emulsions of sulfuric acid in kerosene, carried out with a high-tension alternating potential, proved that droplets of sulfuric acid (having a high dielectric constant) are drawn toward the place of the greatest concentration of lines of force in the electric field and then coagulated. Pawlikowski tried to work out a definite control of the electrical method of resolution of emulsions by means of an electric field, so that the conditions chosen would not result in greater dispersion or atomization, instead of coalescing small droplets into larger ones. He postulated the existence of an "optimum voltage" for the resolution of an emulsion, emphasizing the fact that excessive potentials would cause a secondary atomization of the already coagulated conducting liquid. Experiments proved that by exceeding the "voltage limit" an emulsion was formed, and that a slow decrease of the voltage reversed the emulsion to the original state. The potential gradient in the field, rather than the total potential difference between the electrodes, is an important factor in electrical dehydration. Hence the potential to be applied depends upon the potential gradient desired and the distance between the electrodes.

Pawlikowski proved also the dependence of the coagulation process upon the degree of dispersion. Electric dispersion on the other hand, among other factors, was found to be a function of the interfacial tension, magnitude of the potential gradient, of the distribution and the potential of the electric field.²⁸⁵ Thus, as pointed out, the action of electrostatic forces causing the agglomeration and subsequent subsidence of the disperse phase in an emulsion depends upon the potentials and the dielectric constants of the components of the system, and likewise upon the non-uniformity of the electric field.

Pawlikowski carried out experiments in order to find the optimum conditions for the deformation of the electric field. He assumed that introduction of crevices or drilling small holes of different diameters into the electrodes may assist in the coagulation process. All processes occurring with plain electrodes were the same as with perforated electrodes; but, considering the electrodes as condenser linings, an increase in the capacity takes place only in the case of perforated electrodes. Because of this, the suspended globules of the disperse phase are sucked into the perforations and there they extend into a film covering the perforated part of the electrode. This phenomenon depends upon the spacing between perforations, the interfacial tension of the suspended liquid in comparison to the liquid in which it is suspended, the potential between the electrodes and their distance apart.

It was ascertained that use of a fine wire gauze for an electrode, with proportionally small apertures, instead of a perforated sheet metal, gave results similar to those obtained by using electrodes from solid sheet metal having the same dimensions, the voltage being 10,000 volts and the spacing of electrodes equal to 10 mm. The area of perforations, their spacing, their distance apart, and the total ratio of the metallic area to the area of perforations are factors to be considered. The agglomeration of the suspended particles takes place in the form of chains or streamers extending from one electrode to the other; simultaneous formation of an excessive number of those chains, causing a temporary short circuit accompanied by a waste of energy, should be prevented.

The inner electrode is often rotated with reference to the outer. The settling of water globules was improved by constructing the electrodes in a conical shape; thus the water particles had a short distance to travel in their descent before coming into contact with the wetted septum surrounding the outer electrode.⁹⁵ The septum used most effectively adsorbs them, offering the collected water a continuous channel downward through the oil.

The pioneer in electrical treatment of oil-field emulsions was Cottrell.⁹⁶ Electric processes for dehydration have been operated either with alternating or direct current. The two processes, while often confused, are entirely distinct. One involves cataphoretic separation, accompanied by coalescence, of the emulsified water droplets under the directional influence of a direct-current field, whereas the other involves coalescence, accompanied by accelerated gravity separation, without cataphoretic

motion, under the electrostatic inductive influence of an alternating-current field. It is thus seen that the fundamental phenomena upon which the processes are based are entirely different. In the case of direct current, as claimed in the patent of Seibert and Brady,⁴⁶⁸ the process depends upon cataphoresis, or electrical migration. Sherrick and Jones,⁴⁷² studying cataphoresis of colloids, based it on the migration of colloidal particles when subjected to unidirectional electrical stress. Application of an external electric field causes motion of the suspended particles, because charges of one sign are "bound" to the particle, while those of the opposite sign are "free" in the continuous phase.

The electrical process with direct current consists in passing the emulsion between electrodes connected to a source of a direct current having a potential of 250-260 volts. The current varies from 3-5 amperes. Some electrolysis doubtless takes place, since the electrodes are about half an inch apart, so that at times considerable current passes.

In the case of demulsification of water-in-oil emulsions with an alternating current, there is no steady migration toward either electrode. The field is continually reversing. The only tendency left for the irregularly distributed dispersed particles is to arrange themselves along the lines of greatest field intensity. The electrostatic field intensity is a function of the arrangement and spacing of the electrodes, as well as of the haphazard arrangement of water droplets in the oil, since this alters the "permeability," *i.e.*, the dielectric constant of the material in the field, from point to point.

When a crude-oil emulsion is subjected to the influence of a high-potential electric field, each dispersed emulsion particle, being conductive, becomes charged by induction. The charge is retained by the droplet as long as the electric field is applied. The coalescence results from the mutual attraction of adjacent emulsion droplets which, under the action of the applied electric field, line up between the electrodes, with oppositely charged portions of adjacent droplets in close proximity. The electrostatic attraction between the droplets suffices to rupture the separating films as droplets come into contact with one another. The joining of adjacent droplets continues until the resulting water drops are large enough to settle out of the oil by gravity.³⁸⁵

The Petroleum Rectifying Co.,³⁸⁴ operating under various patents covering electrical dehydration, has installed a number of plants in California, Texas, Louisiana, and Arkansas, as well as a few in Oklahoma and Kansas. Two types of dehydrators were in general use at that time (1923), the National type and the Cottrell type. The Cottrell treater was the first type of electrical dehydrator ever put to commercial use (1909), and the patent was issued to Cottrell in 1911.⁹⁵ The National type treater described by Harris²¹⁴ consists of a closed tank 8 feet in diameter by 15 feet high having vertical plates serving as electrodes. There are alternate plates grounded to the tank and the remaining plates are hung from insulators and connected to a high-voltage transformer,

11,000 volts being customarily applied to them. These plates are spaced from 6 to 8 inches apart.

The oil to be treated enters the lower portion of the tank through a pipe and passes between the electrodes. The clean oil is drawn off the top to a shipping tank and the water settles to the bottom and passes out through the gooseneck water bleeder. The tank is kept full of fluid at all times during treatment. A body of water, varying from one to about six feet, is usually maintained in the tank, its presence being an important feature of the operation.²¹⁴ The Cottrell type of treater is one in which each unit consists of a galvanized metal tank about 3 feet in diameter at the base and 10 feet 7 inches in height. The shell of the tank forms one electrode, and circular plates, mounted on a vertical shaft and slowly rotated by means of suitable gearing, form the other electrode. The tank forming one electrode is grounded, and the rotating electrode is insulated and connected to a source of high-voltage alternating current, usually 11,000 volts. The emulsion is fed into each unit or treater at the top and passes down through the treater, where it is drawn off at the bottom, and led to a trap or separating tank where the water settles. The dry oil is drawn off the top of the separating tank through an adjustable swing pipe, while water is bled from the bottom. The capacity of each dehydrator unit on the average is 300 to 1000 barrels of oil per day. The electric energy consumption ranges from 5 to 75 watt hours per barrel of dehydrated oil. The cost of electricity averages one cent for 20 to 50 barrels. The plant utilizes a single transformer and motor and a single settling tank, and may consist of any number of treater units from one to eight in even multiples. The two types of treaters are fundamentally different in every detail of construction and in every principle of operation. They are alike in but one feature, and that is that both employ the demulsifying action of a high-potential alternating electrostatic field.

The National and Cottrell type dehydrators were the only ones in general use about 14 years ago. The chief types of dehydrators now used by Petroleum Rectifying Company are as follows: HF, CF, DTCF, HODTCF, HS, DTHS, CR, and DTCR. The operating principles of the modern dehydrators are different. Early practice has shown that in treating certain types of emulsions the rotating electrode is essential to prevent continuous short circuits. In modern types of treaters, short circuiting is prevented by control of hydrodynamic and electrical characteristics. The heating of emulsions prior to electrical dehydration has its advantage, but is usually carried out in closed systems and is limited to temperatures ranging between 150 and 180° F. When electricity is passed through oil, it is not heated to any appreciable extent. The distance separating the electrodes in dehydrators is usually governed by the water content of the oil. The electric energy consumption per treater is remarkably low, varying from 6 to 15 kilowatt hours per 24 hours. This consumption represents an average cost of about 40 cents per day, based on the rates in the Gulf Coast fields of 4 cents per kilo-

watt hour. The average cost of operating a one unit Petreco plant in one Texas field, recovering one thousand barrels of net oil, is \$26.20 per day, or 2.6 cents per barrel. The records of the Petroleum Rectifying Company show that the cost for electricity is of the order of 0.05-0.10 cent per barrel of pipeline oil produced.³⁸⁶ The dehydrating capacity of the treater varies, depending on the character of the emulsion to be treated. An average of 1500 barrels per 24 hours can be treated in a National plant, whereas almost 2500 barrels per 24 hours can be dehydrated in a six-unit Cottrell plant. The percentage of water and emulsion in the oil is usually not a determining factor in the capacity of the treater. In the case of emulsions varying in gravity from 11° to 40° A.P.I., having a water content as high as 80 per cent, it is possible to dehydrate the emulsion to a water content of less than one-half of one per cent, while the entire crude production is restored to its original gravity.

Equipment and Methods Used in the Electric Dehydration of Crude Oil Emulsions

Many types of electrical equipment and many processes of electrical dehydration have been patented and described in the literature. Some of them are cited in order to show the technical development of the application of electricity to dehydration. In the field of electrical dehydration of emulsions, the commanding position belongs to the Petroleum Rectifying Company of California. That Company owns some 200 or more patents in this art of dehydration and is the only company in the United States now engaged in electrical dehydration of crude-oil emulsions. The conventional process of electrically resolving crude-oil emulsions involves pumping the emulsions into storage tanks, withdrawing them subsequently from these tanks and subjecting them to the action of an electric field to coalesce the dispersed particles. Pumps used in oil fields and around dehydrating plants are usually of the reciprocating steam type. These pumps can be operated at variable speed, and since they are of the positive displacement type, they do not cut the emulsion to any great extent. The bucket type of rotary pump and the rotary gear pump, for example, are of the positive displacement type. They have a relatively slow speed (200 R.P.M.) and give little agitation. Pumps that are used to feed electrical dehydrators should not only be of the positive displacement type, but should also be capable of pumping a variable volume of fluid controlled by the speed of the pump. Centrifugal pumps, which are not positive displacement pumps, should never be used for dehydrator feed pumps. When operating against pressure, there is some slip in the pump; therefore these pumps cut emulsions badly. In general, the tighter emulsions are the more difficult to dehydrate and pumps causing the least amount of re-emulsification should be used.⁶⁴⁹

McNear and Bowles³³⁷ (Petroleum Rectifying Co.) dehydrated oil electrically in a tank having an inner conducting surface and provided with a number of annular electrodes spaced axially and connected to

a source of electrical energy and to the conducting surface. Between the annular electrodes a series of disc electrodes is spaced axially from the annular electrodes and connected to the other side of the source of electrical energy, leaving a space for the flow of liquid through the successive annular electrodes and around the successive discs. The spaced electrodes of opposite polarity may be arranged more closely together at the top than at the bottom of the tank.

McKibben's³³⁵ (Petroleum Rectifying Co.) apparatus for the electrical separation of emulsions consists of a container having an inner concentric vertical tube projecting upward through its base to about half of its height and open at the top. The container is closed at the top, and an adjustable electrode projects vertically downward into the central tube. A valve, which permits gas to escape at a predetermined pressure is also provided on the upper part of the container.

Slonim and Beklemishev^{478a} describe an apparatus used in the dehydration of petroleum emulsions by electric fields of high frequency. This apparatus differs from the Cottrell dehydrator chiefly with respect to the following factors: (1) one electrode is separated from the emulsion by a solid dielectric layer. The rotating internal electrode, consisting of a wooden cylinder provided with 8 thin metal strips placed crosswise and connected at the ends, is placed in a Bakelite cylinder, surrounded from the outside by a brass cylinder serving as a second electrode; (2) the emulsion is introduced from the top in the Bakelite cylinder and is led off from below; (3) the dehydrator must be filled completely and be free from gas bubbles. The internal electrode and one pole of the transformer are earthed; the outside electrode is connected by a self-induction coil with the other pole of the transformer, and parallel to it is built a spark discharge within a displaceable distance. The primary voltage is 110 volts, the secondary voltage 36,000 volts. The emulsion is resolved at 30-40°; the remaining moisture of the oil is $\frac{1}{2}$ per cent water; electric energy exclusive of pumping is 0.8-1 kw/hr. The time required for separation of the water is 3-6 hours. At the bottom of the separator water, petroleum, and the residual coarse, dispersed, unstable emulsion precipitate in layers. The apparatus is used on a semi-industrial scale.

The HF type Petreco dehydrator has a capacity several times greater than the Cottrell treater, the average varying between 1000 and 3000 barrels per day per treater, depending upon the character of the wet oil. The average secondary voltage applied by the transformer of this type of treater varies from 11,000 to 16,000 volts, depending upon line conditions, percentage taps used, reactance coil and auto transformer coil settings. There is one feature, namely, the motor-driven reduction gear for moving the live electrode up and down within the dehydrator.

One very interesting modification of the electrical equipment is found in patents issued to de Brey,^{38, 64} who discovered that certain oils are more successfully treated when peaked voltage effects are applied to the oil, a special generator being developed for this purpose. de Brey suggested treating mineral oil emulsions in successive steps at increasing voltage,

depending upon the degree of dryness of the oil. He states also that the smaller the water particles, the higher the electric pressure required to separate them from the oil. Consequently, in order to obtain complete dehydration of an emulsion, an electrical pressure of 10,000 to 50,000 volts may be necessary.* However, the installation and operating costs of this dehydration method do not permit its general use. The chief reason, however, for not using the de Brey process (U.S.P. 1,591,472) is that it is unnecessary, as conventional and simpler methods meet all commercial requirements satisfactorily.

Dameron¹⁰¹ described electric dehydrators (HF) which treat emulsions from the Gulf Company, Texas Company, Natural Gas and Fuel Corporation and Danziger wells. Each of the dehydrators operates independently, being controlled automatically to prevent explosions. The pumps and heaters also operate independently. Inside the dehydrator tank an iron rod is suspended from the top of the tank. Three large insulators are inserted in it near the top. Below the insulators the upper electrode, having a conical shape, is attached to the iron rod. Directly beneath, a few inches below, is the lower electrode, a metal cone, whose edge has a one inch clearance from the tank. A transformer is mounted on top of the tank, the high-voltage wire being connected through an insulator bushing in the top of the tank, to the upper electrode, while the other wire is grounded to the side of the tank. Alternating current enters the transformer at 220 volts and is stepped up to 11,500 volts before being delivered to the upper electrode. Wyant,⁶⁵⁷ working on heavy-oil emulsions and dehydrating them to a water content of 2 per cent, found that the rate of feed must be slowed down so that each pair of treaters produces not more than 1200 barrels. The electrodes must be set wide apart on the first units and close together on the second units, the oil being treated in two stages.

Segal⁴⁵⁷ describes an electric dehydrating plant which is essentially a huge Leyden jar whose disruptive discharge penetrates the oil film and allows the water particles to run together. In practice, an alternating current is stepped up by a transformer to about 10,000 volts. The plant has a capacity of 500 barrels a day. The oil treated formerly contained 14 per cent of water, which has been reduced to less than 2 per cent. The electrical current was stepped up to 10,000 volts and experiments showed that it required about 1 to 7 watt hours per barrel of oil treated. W. O. and H. C. Eddy¹²⁵ patented an electric dehydrator, recommending that the crude emulsion be led continuously into a tank built of $\frac{1}{4}$ -inch sheet steel and that it be dehydrated while passing between two flat or conical sheet-metal electrodes with a potential difference of 11,000 volts (alternating current of usual frequency). The emulsion may be agitated if desired by reciprocation of one electrode which causes a sloshing motion of the fluid.

Three patents on dehydration processes were issued to Laird and

* American rights to these patents are the property of the Petroleum Rectifying Company.

Raney.²⁹³ In the first, petroleum emulsions are separated by treating them with an electric current in a cylindrical shell, divided into an upper and a lower compartment by a pan, in which hollow electrodes are fixed, forming an open communication between the compartments. On the inner walls of these electrodes there is a series of inward projections, and inner electrodes with projections on their outer surfaces are placed in each of the outer electrodes. In the second, the emulsions are treated with a current of high alternating potential successively impressed between a number of pairs of electrodes. Means are provided for varying the effective diameter of the inner electrodes. For this purpose they are made of slotted pipes surrounded by springs engaging a series of blades projecting through the slots, a central rod carrying a series of cones, which are moved within the pipe to expand the blades. In the third, an alternating electromotive force is connected with or disconnected from the electrodes by means of a distributor driven by a synchronous motor in order to utilize a certain portion of the potential at each alternation.

Dehydrators, Inc.¹⁰⁶ patented a process for treating emulsions with a high-tension alternating potential. The potential and/or the distance between the charged electrode and the container wall are such that the earthed container wall is outside the zone of charged water particles present around the electrode. The formation of convection currents is prevented; therefore, discharge of the charged water particles does not take place at the earthed wall of the container. The equipment for dehydration of petroleum patented by Quinby⁴²² consists of an electrode made of two concentric metallic cylinders. In the annular intermediate space a movable, concentric, cylindrical electrode is inserted. The oil to be dehydrated is passed through the annular space and is subjected there to the action of electricity.

Fanto and Shitar¹⁵¹ describe a method for electrical clearing of an emulsion. They operate with a direct current (at 220 volts and a lamp resistance); two wires reaching below the surface of the emulsion are moved about in the liquid to be cleared.

When a spark discharge is employed, one terminal of the induction coil is connected to a wire around the neck of a separatory funnel, the edge of which is moistened with water, or to another conductor; the other terminal is connected with a loop of a wire passing through the cork closing the funnel and dipping into the emulsion contained therein. The Bataafsche Petroleum Maatschappij³⁶ separates crude-oil emulsions by means of high-voltage, rectified, single or poly-phase current. Patents on the use of poly-phase alternating current have been issued to McDonald³³² and Hanson.²¹² German Patent 431,222 Kl. 23b, Gr 1, July 5 (1926) relates to the precipitation of the ingredients of a petroleum emulsion. The method is characterized by the use of a pulsating, interrupted, symmetric or asymmetric alternating current. It is claimed that this invention has the advantage of resulting in quick separation, due to the rapid succession of short current impulses. Kroch²⁷⁹ char-

acterizes the Cage process as different from the Cottrell process. 50,000 to 66,000 volts are used. There are two electrodes, one of which is the central rod, while the other is the tank wall. Current flows between the electrode and the tank wall. The dehydration takes place in the space immediately surrounding the rod electrode; it is called the "zone of space charges." The concept of "space charges" on which Cage based his process does not apply to such impure systems as crude-oil emulsions. Gemant ¹⁷⁶ showed that space charges cannot exist in dielectric oils unless the latter are of extremely high purity. In practice, the method is applied for dehydration of coal tar and brown coal tar.

Wilcox ⁶³⁷ described a Cage dehydrator which has been operated on the Pacific Coast. This dehydrator has a special regulating transformer which automatically regulates the applied voltage in an inverse ratio to the conductivity of the oil. Thus overloading of the transformer or of the equipment is prevented. This method has an entirely new principle. The plant control centers in a valve actuated by the kinetic energy of the moving stream and is independent of the fluid level. There is also a new type of inlet bushing for high voltage. This dehydrator has a greatly increased capacity; a unit handles 4000 to 5000 barrels per day. The total current consumption for all purposes (except the operation of pumps) for two units treating 6000 barrels of oil per day is 35 to 50 kilowatt hours per 24 hours. The plant operates with best results at 140-145° F, whereas other dehydrators require a temperature of 180-190° F. The radiation heat loss of a Cage dehydration plant is about the same as that of other dehydrators operating under comparable conditions.

In this dehydrating system, in addition to the charging current, a current also flows back into the transformer. The line current at the usual 220-volt distribution voltage, was of the order of 15 to 45 amperes (corresponding to 0.05 to 0.15 ampere in the high-tension circuit).

Dehydrators, Inc. (Cage ^{100a}) patented an apparatus for dehydration of water-in-oil emulsions, which comprises a suitable tank with provision for passing an emulsion through it, and a series of electrode sets arranged in the path of the emulsion flow. The spacing of the electrode sets is progressively diminished in the direction of emulsion flow; and this diminution is directly proportional to the decreasing conductivity of an emulsion as its relatively electrical conductive component is progressively removed. In this apparatus means are provided for applying to the electrode sets as a whole a potential varying inversely as the total conductivity of an emulsion flowing between all the electrode sets. This includes an instrument actuated by the current flowing through the emulsion, and voltage control circuits are regulated by this instrument. Details of an apparatus and its operation in electric dehydration of petroleum emulsions have been described in a United States patent.^{383a}

Land's ²⁹⁴ (Petroleum Rectifying Co.) dehydrator has a horizontal surface, fixed in the emulsion receiver, to which is attached a series of disc electrodes having between them solid electrodes of opposite polarity.

The Bataafsche Petroleum Maatschappij³⁷ subjects the emulsion to an oscillating discharge of high-frequency currents. Dijxhoom removes emulsified lubricating oil from condenser water by passing a 110-volt current through it as it flows through a feed pipe. Gerlach¹⁷⁹ devised an electro-osmotic process for separating the solid constituents from an emulsion, electro-osmosis being effected by means of a cylindrical anode rotating between surrounding cathodes constructed in sections, to each of which the current is conducted separately. One of these sections connected with a hopper approaches very nearly the direction of the rotation; and those sections affecting the subsequent dehydration are pressed by means of springs against the layer of partially dehydrated material on the anode.

Mazetty³²⁷ discussed the electro-osmotic dehydration of tar. His apparatus consists of an exterior receiver containing water and a copper cathode. Tar is poured into the porous interior container holding a positive electrode. A voltage of 275 and an amperage of 0.06 is required and a temperature of 45-50° is maintained. The water content drops from 8.7 to 1.0 per cent within 12 hours. The waste of the light oil is 0.3 per cent. Tar with a high water percentage, 15.36 per cent, gives the same degree of dehydration, but a larger waste in the light oil, about 1.1 per cent.

Structural changes introduced into electrical dehydrators by Hanson²¹² prevent electrical breakdown of an insulator located in a chamber in a dehydrator by introducing carbon dioxide under pressure into the chamber. From time to time the chamber is flushed with carbon dioxide to remove the gases given off by the crude oil. Van Loenen's patent³⁰⁸ covers a method of, and an apparatus for, electrical dehydration of emulsions, in which dielectric breakdown is avoided by use of a gas barrier in the treating field. The electrodes consist of a rod electrode coaxially disposed within a hollow cylindrical electrode. The electrodes are positioned within a gas-filled chamber and the emulsion is allowed to flow downward along the surface of the rod electrode in a thin layer, being subjected to an electric field of high intensity, and to the bombardment of ionized gas molecules.

H. C. Eddy and C. F. Kiech¹³³ patented an electric dehydrator with an emulsion guiding surface. The live electrode is in the form of a vertical sleeve submerged in the treated oil, and the water-in-oil emulsion is fed axially in the form of a solid stream, which impinges upon the pointed end of a vertical rod of insulating material and forms an annular stream. In an alternate form the sleeve electrode may be almost horizontal and the emulsion guided along the axis by a trough.

Petroleum Rectifying Co. (Eddy¹²⁹) applied electric treatment in dehydrating emulsions by subjecting them to the action of an electric field in which the emulsion separates into its respective components. The electric treater used has as its particular object the prevention of dielectric breakdown by using a dielectric barrier of dry oil. The principle is, to a certain extent, analogous to van Loenen's patent mentioned

above, and provides a dielectric barrier of gas. Garrison¹⁷¹ dehydrates petroleum emulsions by introducing them tangentially into space between co-axial conical electrodes, so arranged that their apexes are directed downward, and the potential gradient of the field increases in the direction of flow of the emulsion.

Fisher (Petroleum Rectifying Co.³⁹¹) breaks emulsions by subjecting them to a non-uniform electric field between concentrically arranged electrodes. The emulsion stream is sprayed into the field with high velocity, the injector action of the streaming emulsion being used to induce a circulation of dry oil between the electrodes, so as to form a dielectric barrier in the weaker part of the field. The emulsion stream and the dry oil in the induced stream flow through the electric field without substantial mixing.

Electric dehydration of emulsions such as those of crude petroleum has been carried out by Adams and Barlow by passing the emulsion in a continuously flowing stream longitudinally through the annular space between a cylindrical outer electrode and an inner electrode tapering inward in the direction of the emulsion flow. The phases of the emulsion are subsequently separated from each other when a continuous flow of electric current is passed between the electrodes and through the stream.

Girvin¹⁸² claims that an emulsion in which the continuous phase is a petroleum product and the disperse phase an acid or an alkali may be treated by subjecting it to the action of a uni-directional electric field of several thousand volts per inch, which is of great intensity adjacent to the negative electrode. The particles of the disperse phase are cataphoretically separated from the oil and deposited upon one of the electrodes, from which they are removed by suitable means.

Siemens-Schuckertwerke A.-G.⁴⁷³ break emulsions by applying high-voltage, uni-directional impulse discharges given to the electrodes of the emulsion breaker with a duration of not more than 10^{-5} sec. The time intervals between successive discharges are at least ten times the duration of each impulse. This method permits application of very high voltages without permitting the passage of heavy currents. In another patent⁴⁷⁴ Siemens-Schuckertwerke achieve separation of emulsions by using a pulsating electric current. The electrodes of the separation apparatus are fed with a pulsating current having a duration of 10^{-5} seconds, or less. Fisher¹⁵⁶ patented a method for the resolution of loose emulsions by pretreating the emulsion electrically between live and earthed electrodes, withdrawing the unseparated oil and water mixture from the middle layer of a settling chamber, which already contained upper and lower separated layers, and pumping this mixture, against a negligible back-pressure, into the water layer, separation taking place by gravity. Fisher¹⁵⁷ discloses in a patent certain structural, electrical and operative details for an electric treating apparatus used in dehydrating natural petroleum emulsions. The emulsion to be broken flows between two electrodes; in order to regulate and maintain the strength of the field and to prevent short

circuiting of the electrodes, a condenser is connected in series with the electrodes.

Petroleum Rectifying Co.³⁹⁴ resolves emulsions by applying a high-tension electric field with a frequency of 60 to 10,000 cycles. Garrison and van Loenen¹⁷³ treat emulsions electrically. The portion of the emulsion not completely separated settles through a series of superimposed coaxial, conical, oil-wetted screens of fine mesh; thus complete and rapid separation into oil and water occurs.

Roberts^{397a} recommends electric dehydration of petroleum emulsions subjected to the action of the electric field set up between electrodes in such a manner that on an alternating potential of primary wave form is continuously superimposed a single alternating potential of secondary wave form, and of higher frequency than the alternating potential of primary wave form, so that a rippled wave form is produced, which is composed of a low-frequency wave, on all portions of which is impressed a single high-frequency wave.

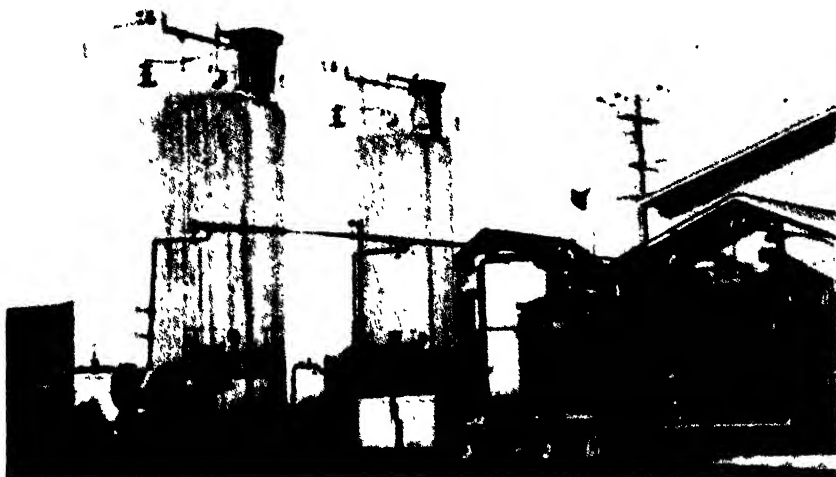


FIG. 28. Two-unit Plant, Elwood Field. Electrodes of the Nozzle Type Are Used in this Installation.

The electric process of treating oil-field emulsions as developed by Petroleum Rectifying Co.¹³⁰ depends for its effectiveness on the difference in dielectric characteristics of the two phases composing the emulsion, oil, which is a fairly good insulator, and salt water, which is a good conductor.

The process consists essentially of a wholly electrical agglomerating step and a purely mechanical separating step dependent upon the difference of the specific gravities of the two substances composing the emulsion. When treating high-gravity, extremely fine emulsions in a CF treater, it has been suggested to inject the emulsion into the electric

field through a system of nozzles at the point of highest field intensity. This is accomplished by using a small rod as an electrode and confining the emulsion to a fluid stream adjacent to its surface. The outer electrode consists of a charged cylindrical shield insulated from and surrounding the rod. A velocity of 40 ft per second or more is maintained on the fluid stream leaving the nozzle. In an HF treater a mechanically agitated type of electrode is used for treating a heavy, slow-settling, viscous oil. The fluid is injected at the center point between two eight-foot, slightly

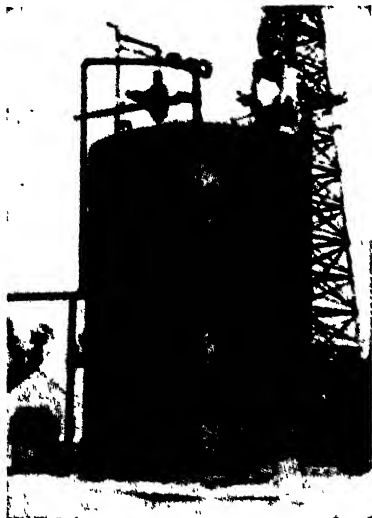


FIG. 29.

Single-unit Dehydrator Employing Mechanically Agitated Electrodes.

conical electrodes. The underside of the upper electrode is provided with a series of concentric rings, so arranged that the intense portion of the electric field is below the edge of the rings beneath which the fluid must pass on its way through and out of the field. With this type of oil, the mechanical agitation is beneficial. A small movement of the electrodes prevents water-rich masses or chains of water globules from bridging the gaps between the electrodes, thus preventing an excessive flow of electrical energy.¹³⁰

The new type of electrode developed by H. C. Eddy, known as the "CR" or concentric ring type, secures cuts lower than any heretofore obtained in the dehydration of California oils.

Passler^{375a} dehydrates an emulsion (from an oil well in Austria), whose water content amounts to over 50 per cent, by passing it through a high-tension electric field. One electrode is a rod, while the other is a cylinder surrounding it. Both electrodes are covered with a dielectric of hard glass. The electrodes are so designed that they present a large surface. The energy consumption is small, ranging from 3 to 15 kw hr per 24 hours of continuous operation (15 kw hr represents a maximum

for emulsions containing 60 per cent of water). To reduce the viscosity, the emulsion is preheated to 50-70°.

The electrodes used in electric dehydrators are now generally either of the horizontal, concentrated-field type, consisting of a nozzle which jets the emulsion along an electrode rod located inside a live shield, or of the concentric-ring type, suspended from supporting brackets. In the latter, the emulsion may be introduced below the electrode unit, rising through the high-potential field, or in a horizontal plane directly into the electric field by means of a radial distributor (Roberts and Worthington, Petroleum Rectifying Co.^{160a}).

Prutzman ⁴¹⁹ patented the electric dehydration of oil in a shell divided into two chambers, upper and lower; tubular grounded electrodes passing through the partitions are the sole means of upflow; the live electrodes are thin wires axial to the tubes. Drains for water are provided from the upper to the lower chamber; through these the emulsion is prevented from flowing. The shape of the live electrode is conical, with closed apex downward. The earthed electrode is a wire screen around the cone, and is supported by horizontal plates from the shell wall; direction of flow is controlled.

Crude-oil emulsions are either treatable or untreatable by the electrical process. Some emulsions are treated with great ease, while others can be treated only by using, in addition to electric treatment, aids such as chemicals, recirculation through the electric field, heat, etc. The Mid-Continent oils are an example of emulsions which cannot be treated by the electrical process. The disperse phase of any natural emulsion is electrically charged, either positively or negatively. In some emulsions, these charges remain as a fixed magnitude; in others they change with age. The change is either in magnitude or sign, or both. If emulsions contain particles which change essentially the magnitude of their charges, or which reverse their charges upon aging, they do not respond to electric treatment after aging; whereas in the opposite case this treatment is highly effective. To secure successful results by the electric process with emulsions for which the aging process proceeds relatively fast, it is necessary to treat the emulsion soon after it is formed. Not more than 6-48 hours should elapse before it is exposed to the action of the electric field. The temperature at which the treatment is performed should be below that necessary to vaporize the aqueous phase of the emulsion. On leaving the well, the emulsion to be dehydrated is transferred under pressure of the pumped emulsion directly into the electric dehydrator. With a flowing well, pressures many times higher than atmospheric are available, and may be utilized in developing higher pressure in the electric treater. High pressure tends to retain dissolved gases in the emulsion, thus further facilitating the electric treatment.³⁰⁶

The fundamental object of another patent by Roberts ³⁰⁷ is to treat by electric methods emulsions which are otherwise untreatable, or difficult to treat, by subjecting them to the action of an electric field even before they leave the well and before they become untreatable because

of aging. An electric field is established in the well from which the emulsion is obtained by positioning a charged electrode in the emulsion stream rising in the well. The dispersed particles of the emulsion agglomerate, and the treated emulsion moves upward to the top of the well into a separating chamber, where the phases are withdrawn separately.

Electric dehydration of petroleum emulsions is effected by applying the emulsion to the surface of an electrode where it falls freely upon a second electrode. From the first electrode an edge discharge is established in the direction of flow of the emulsion. An intense electric field is maintained between the electrodes. The falling stream of emulsion is thus subjected to a high potential gradient, resulting from the electric field.¹¹¹

Electric treatment for dehydrating petroleum emulsions may be carried out successfully when a number of condensers are successively charged and discharged through a pair of electrodes in contact with the emulsion to be treated. Each condenser is isolated from the charging source during the discharging interval.¹¹²

The Petroleum Rectifying Co. (H. F. Fisher³⁹²) adapted the principle of dehydrating water-in-oil emulsions by leading them from below through an electric field; the precipitated water droplets thus pass downward through the emulsion and pull along further amounts of water from it. The breaking of water-in-oil emulsions by coagulation in an electric field is carried out in an arrangement permitting adjustment of the field ratio required for emulsions of different density.⁴⁰¹

Woelflin's⁴⁰³ method of electric dehydration of crude petroleum emulsions involves changing the emulsion into a low-density foam comprising masses of non-condensable gas, surrounded by thin films or layers of the emulsion in an electric field between electrodes associated with an insulating means; the foam is subjected to the action of the electric field. This method provides treatment of the gas-emulsion mixture both directly by the electric field and indirectly by the ionizing action of the electric field on the gas mass. A flowing stream of a dielectric liquid along the insulating means prevents contact between it and foam.

The petroleum emulsion to be treated is flowed downward through an elongated, vertical, interrupted electric treating field; gas is injected into the emulsion as it flows, and is allowed to rise through it.⁶¹²

Oil-in-water and water-in-oil emulsions may both be treated by subdivision into minute liquid particles separated from one another by a gas. The gas acts as a dielectric barrier to prevent excessive current flow between electrodes, and furnishes at the same time a low-viscosity medium. Then an electric field of sufficient intensity is established to ionize the gas. The emulsions to be electrically treated are introduced into the electric field in an atomized state. The atomizers used are such as to break up the liquid by centrifugal or mechanical force without the use of a high-velocity jet of air or other gas. The atomized emulsion is introduced into a gas-filled electric field of sufficient intensity to

coalesce the disperse phase; the coalesced liquid phase is then separated from the liquid forming the continuous phase.³⁸⁹

According to Slonim and Beklemyschew,⁴⁷⁸ mineral oil emulsions are broken by treating them with a high-frequency current.

In the California and Gulf Coast oil fields, the majority of all emulsions are treated by electric dehydration. Fig. 30 shows a cross-section of an electrical treater, operating on the principle that the dispersed or scattered droplets of a petroleum emulsion coalesce and readily settle out from the oil by gravity when brought within the field of influence of a high-potential alternating current.⁶⁵

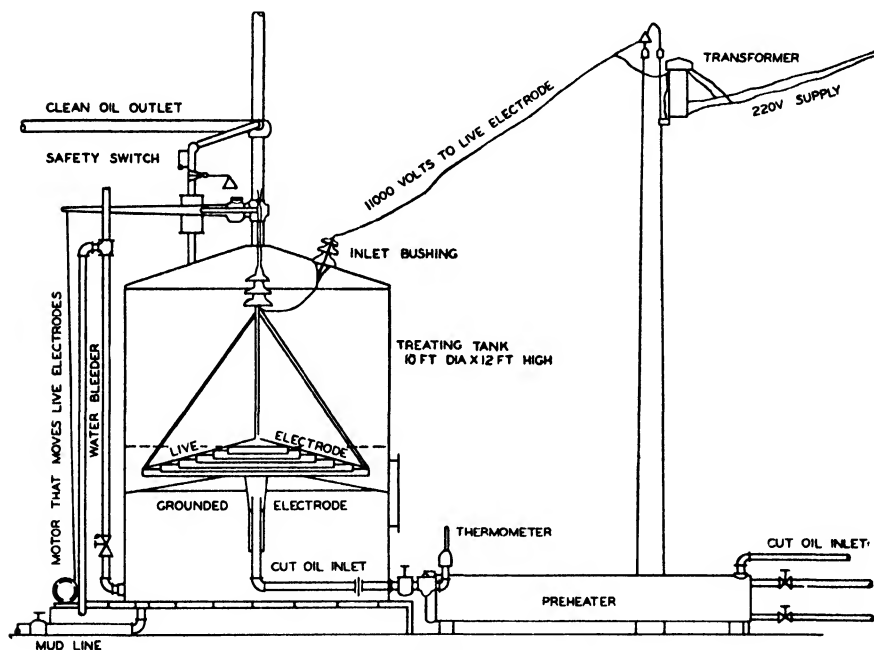


FIG. 30.

Woelflin's⁴⁰² invention provides a pipe-line treater which is connected to a pipe-line in such a way that the emulsion flowing through it is electrically treated before being discharged into a more remote section of the pipe-line or into storage. Such treaters spaced along a pipe-line insure higher velocities through it, because they control the re-emulsifying tendency caused by agitation in the pipe and decrease the viscosity of the fluid. The method of treating an emulsion flowing through a pipe-line involves establishing a number of electric fields placed at intervals along the line. Each of these fields has sufficient intensity to coalesce the dispersed droplets of the emulsion system into larger masses, the emulsion constituents being moved successively through the fields with-

out substantial separation of constituents during passage between fields, and separating after subjection to the last electric field.

When an emulsion contains one phase of a material of high conductivity and another phase of a material of relatively low conductivity, Woelflin's novel method⁴⁰¹ and apparatus for introducing high potentials into an electric dehydrator are particularly applicable. In treating petroleum emulsions, the conducting liquid phase is usually water or aqueous solutions, the other liquid phase being oil of lower density than the water. Thus the water tends to gravitate to the bottom of the tank. When treating certain tar emulsions in which the conducting liquid phase is of lower density than the other liquid phase, the water tends to collect in the upper end of the tank, while the tar gravitates to the lower end. In this instance, if the potentials are introduced through the bottom of the tank, many difficulties will be encountered with leakage around the insulator or accumulation of sludge, increasing the tendency toward electrical failure of the insulator. The leakage is undesirable because of fire hazard, and necessity of draining the entire tank. In the new method potentials are introduced into the tank through the wet zone by protecting the insulator from the material in the wet zone.

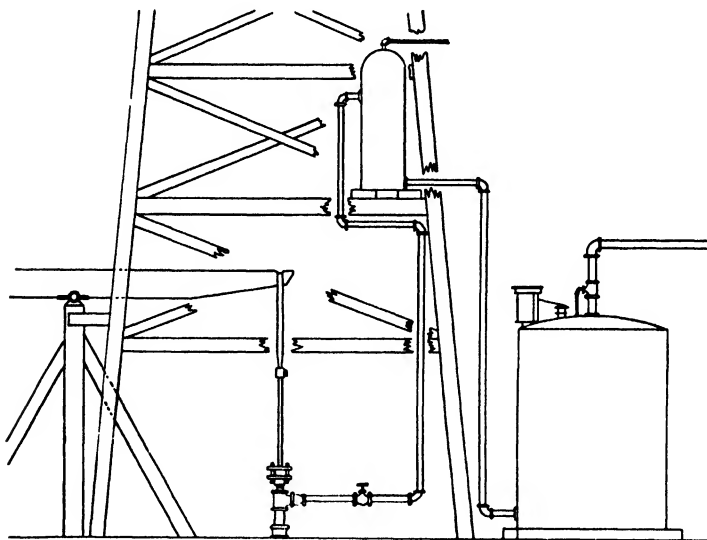


FIG. 31. Diagrammatic Sketch of the Electric Dehydrator.

The high-potential transformer or other current source is located at or on the upper end of the tank. In one end of the treater tank are provided separated bodies of a conducting liquid and a dielectric fluid (liquid or gas of sufficient dielectric strength); through the latter the potentials are introduced into the tank. The insulating means is protected from the liquid of high conductivity by the use of a boot extend-

ing through the latter and opening in the tank interior in a zone wherein the material is of higher dielectric strength than is the liquid of high conductivity. The incoming emulsion is introduced into the space between the boot and the tank. A suitable baffle or deflector guides from the open end of the boot any conducting material which might otherwise tend

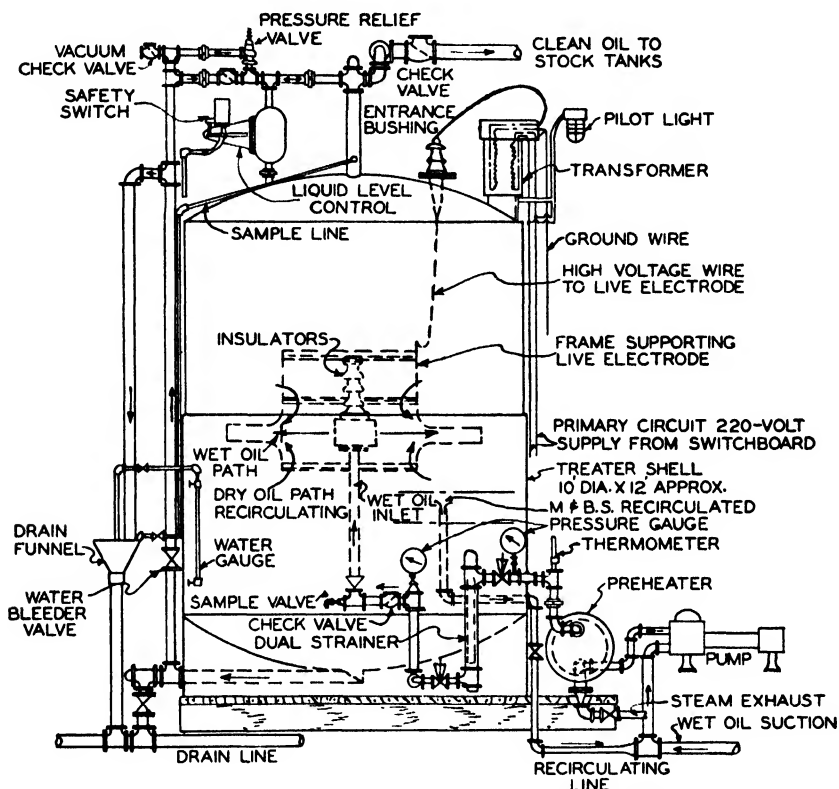


FIG. 32. C.F. Type of Treater with a Capacity of 1500 to 4000 Barrels per Day.

to enter. The dielectric fluid through which the incoming potentials are introduced is continuously dehydrated to maintain the dielectric properties of the fluid.

An electric dehydrator installed at Signal Hill, California, was the first to be operated in California as a flow-line treater, dehydrating the oil as it was pumped from the well without preheating. The oil is produced at 120° F and cuts 61 per cent emulsion and 3 per cent water, or 64 per cent B.S. and water. The treated oil has a gravity of 25.5° A.P.I. at 60° F. Line treaters are now in wide commercial use.

The dehydrator is installed directly beside the derrick. After leaving a gas trap in the derrick the charge flows through a lead line into the bottom of the dehydrator (Fig. 31). The treated oil cutting 0.6 per cent

flows from the top of the dehydrator to the shipping tank without additional pumping.³⁸²

The "Concentrated Field" type of treater developed by the Petroleum Rectifying Co. is shown in Fig. 32. Wet oil passes from the pump through a preheater, then through strainers into a central distributing head. Mounted on top of this head are three insulators from which is supported a framework on which the live electrodes¹⁷⁰ are suspended.

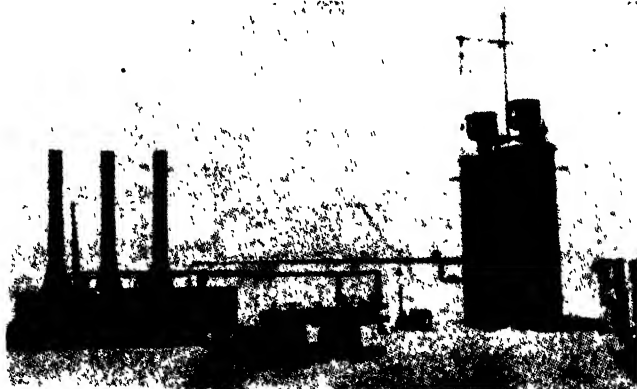


FIG. 33. Cage Type of Treater Used in the Taft Field.

Another type of electric dehydrator uses from 11,000 to 100,000 volts. In this treater, water particles are alternately charged positively and negatively and these seek each other out and coalesce, forming neutral droplets, which are again charged and coalesced until a sufficient mass is formed to settle out by gravity. This treater, known as the "cage type," was formerly in operation in the Taft oil fields. In Fig. 33 at the left are shown three Kelly Dutch-oven type, open-fired preheaters. In the middle are two heat exchangers and at the right two electric treaters.¹⁷⁰

Williams⁶⁴¹ describes the new dehydrating installation operated by the Magnolia Petroleum Co. in the Luling field. It consists of two heating units; each includes a Lucey 100-horsepower, 300-lbs working pressure boiler, and a steam-operated preheater for heating the oil. The oil emulsion is pumped through the preheaters around the outside of the coils. By means of the steam circulating through the coils, the temperature of the emulsion is raised to between 175° and 190° F. A back-pressure of 10 lbs is held on the charge. The temperature of the emulsion in the preheater is controlled by a thermostat on the steam line which automatically regulates the volume of steam passed through the coils of the preheater. Boilers are equipped with automatically controlled water feeds, steam operated. The two steam heating units have a combined capacity of 12,000-15,000 bbls per day. There are six electrical dehydrating units in the installation. Each is operated with 11,500 volts.

From these units the oil is run to a large settling tank, in which the water remaining is settled out.

The electrodes used in modern plants are the horizontal concentric-field (HCF) type and the more recently developed concentric-ring (CR) type. The horizontal-field (HF) type is no longer manufactured, although many of these electrodes are still used in older plants.

The electric dehydrator (Fig. 33a) is a welded, vapor-tight tank containing both a live and a grounded electrode. The voltage is stepped up from a commercial alternating-current circuit in a high-potential transformer (11.5 to 16.5 kw) mounted on top of the dehydrator and delivered

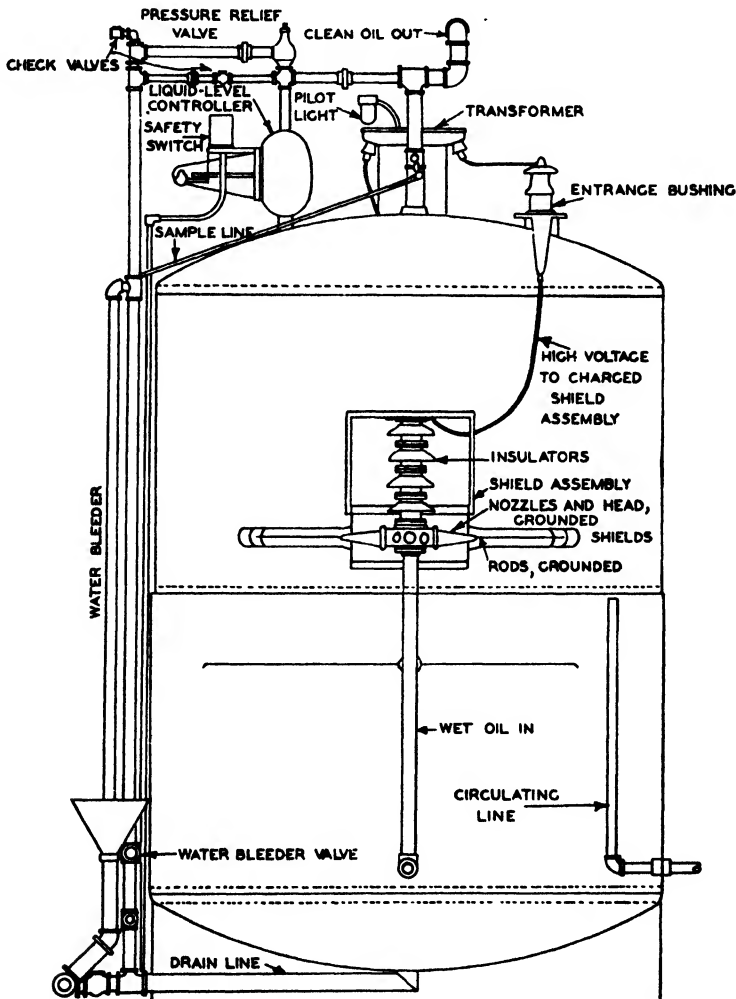


FIG. 33a. Diagram of Horizontal Concentric Field Type (H.C.F.P.) Dehydrator.

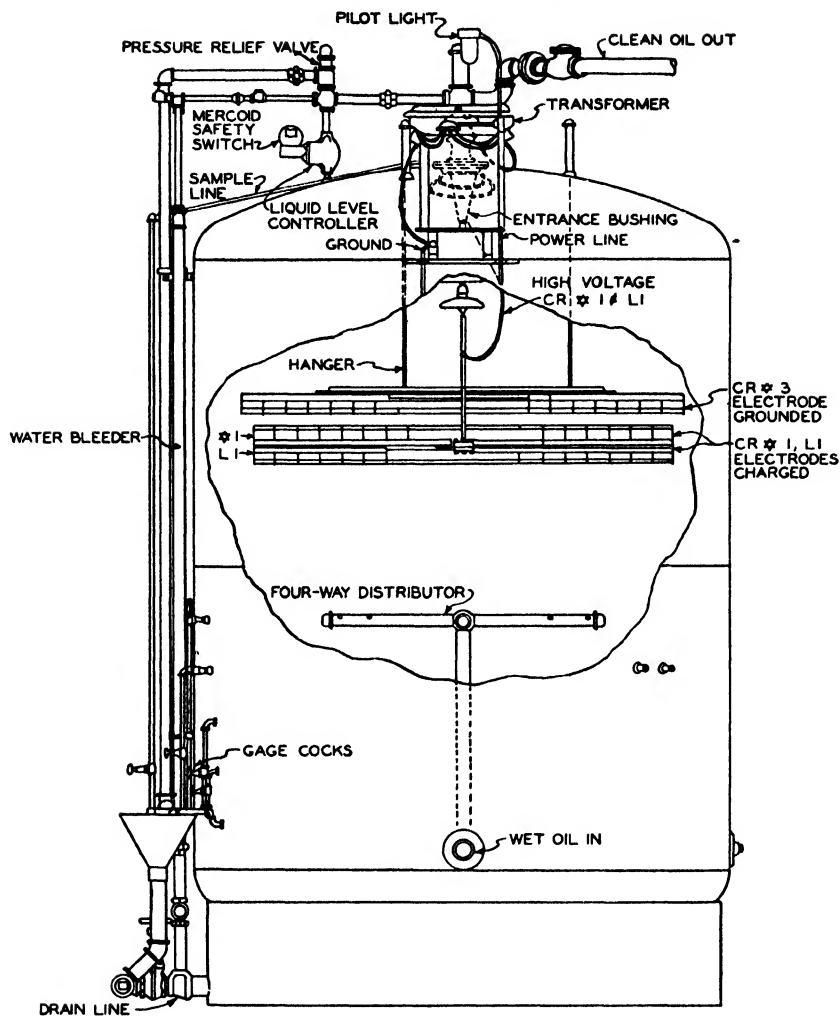


FIG. 33b. Diagram of Concentric-ring Type (C.R.P.) Dehydrator.

to the live electrode through a porcelain entrance bushing on top of the tank. The potential expressed in volts per inch is about 6000, although the total voltage applied may range from 6000 to 100,000. The amount of current consumed is very small—often less than one kilowatt per hour and seldom more than 2 kilowatts per hour. The electric dehydrator used at batch plants is 10 feet in diameter and 12 feet in height and has a volume of about 180 barrels. Throughput capacities range from 1000 to 4000 barrels of clean oil per 24 hours. This size has proved to be the most economical for wells or leases having an output of 400 to 500 barrels of oil per day.

The development of the concentric-ring (CR) type (Fig. 33b) of electrode in its many forms has been one of the important factors in increasing the efficiency of electric dehydration. This type is adaptable to a great variety of oils, particularly to those of heavy gravity. The CR electrode gives lower treated-oil cuts, increased throughput, and more efficient operation at a lower dehydrating temperature than is possible with the other types. It may be operated with one transformer. Two

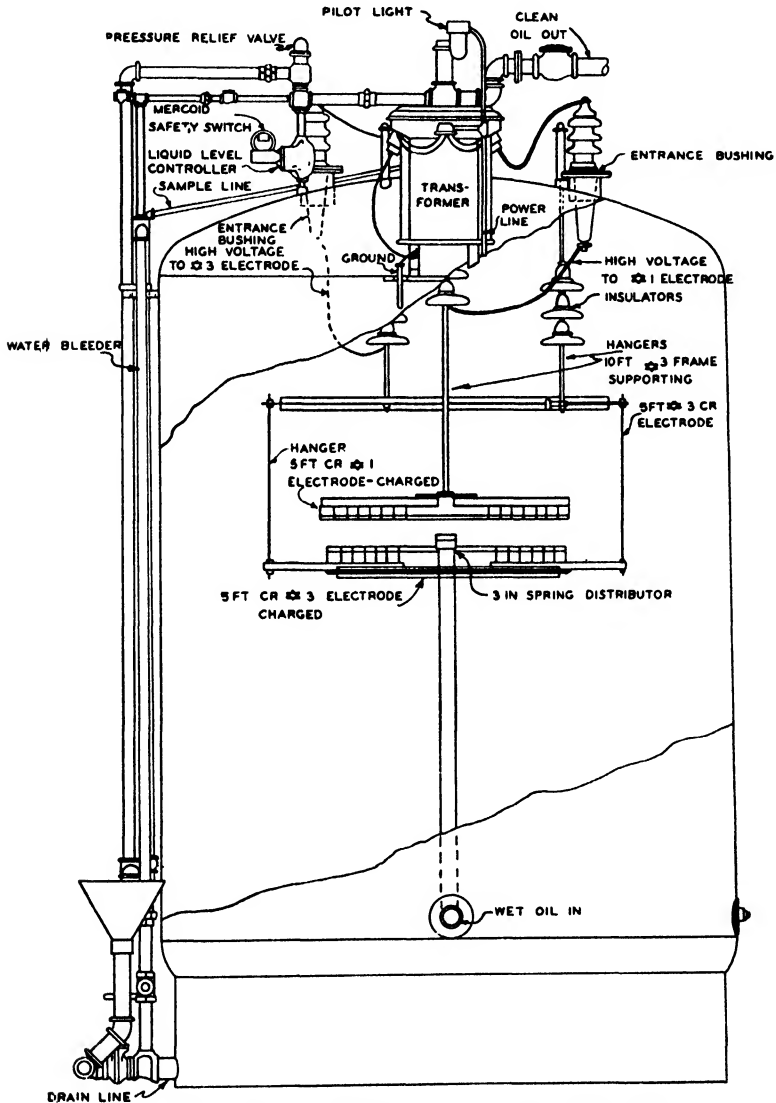


FIG. 33c. Double-transformer Concentric-ring Type (D.T.C.R.P.) Dehydrator.

sets of CR electrodes may be placed in the same shell in order to obtain lower cuts and higher throughput.

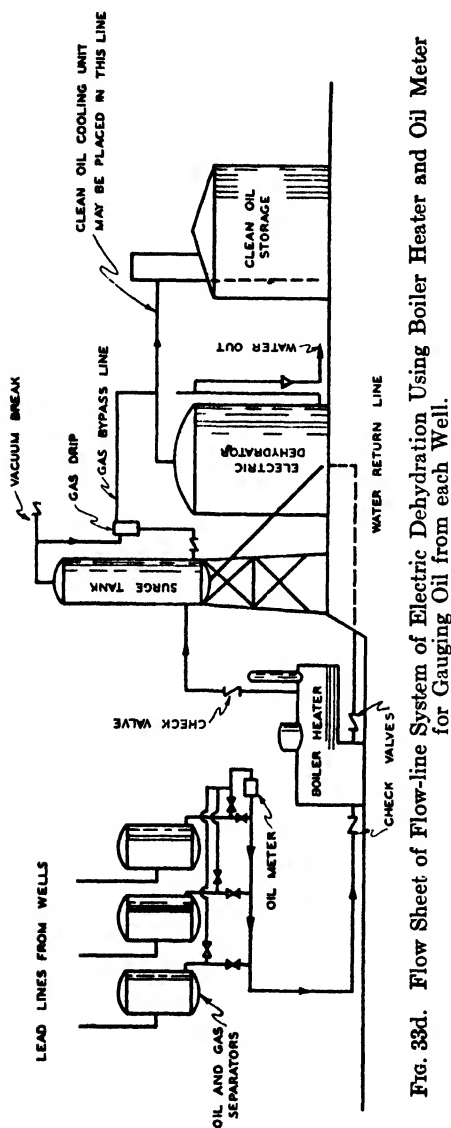


Fig. 33d. Flow Sheet of Flow-line System of Electric Dehydration Using Boiler Heater and Oil Meter for Gauging Oil from each Well.

In the case of the double-transformer concentric-ring type (Fig. 33c), it is possible to maintain a treating field of 33 kilovolts with only 16.5 kilovolts grounded. This electrode, like the HCF electrode, is characterized by turbulence in the treating field.

DTCRP units are used in batch treating of emulsions difficult to

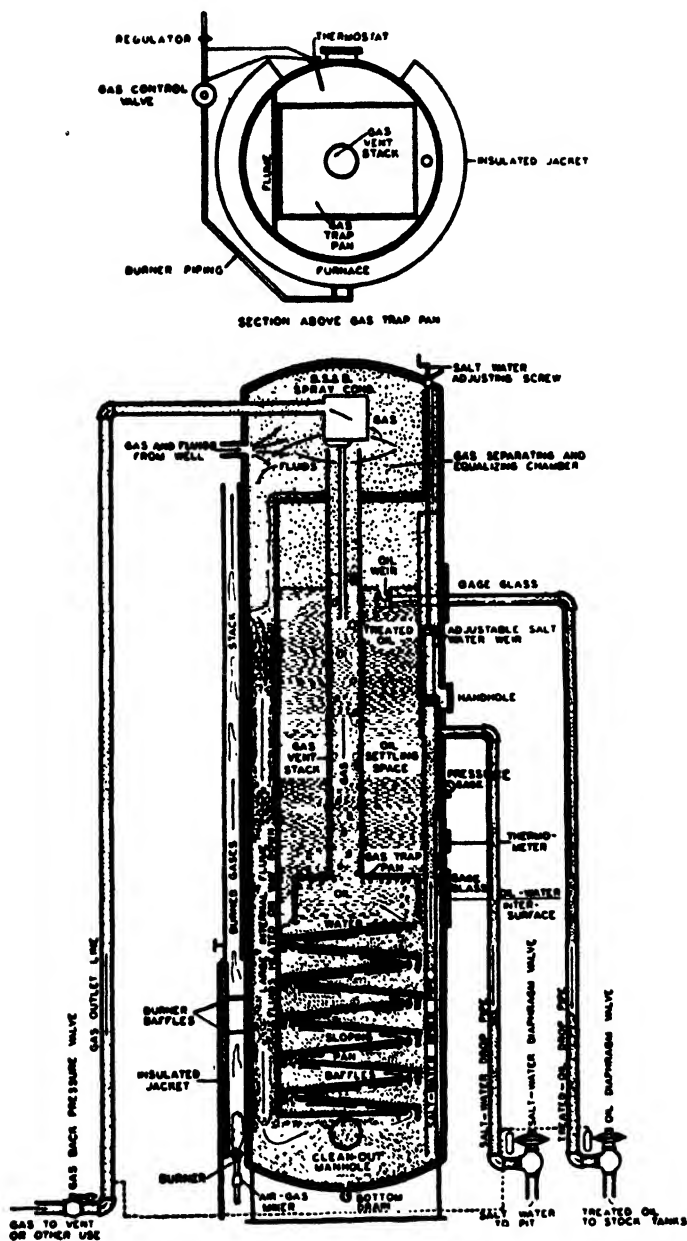


FIG. 33e. Diagram of Automatic Flow-line Treater with External Furnace.

dehydrate, and for conditions under which high-voltage gradients are necessary to cause coalescence.

Mahone ^{316a} states that modernization of central batch-treating plants to incorporate complete heat-exchange equipment, recent developments and improvements in electrode design, and automatic operation of dehydrators are responsible for increased efficiency and reduced operating costs.



FIG. 34. Ten-unit Petreco Electric Dehydrating Plant.

French ^{163a} described a reconstructed central batch plant in California which has a normal capacity of 4500 barrels of clean oil per day. When light-gravity oils are treated, heating of the well fluid may cause evolution of sufficient gas to affect operation of the electric dehydrator. Where this condition exists, an elevated gas-separating chamber is placed between the heater and the dehydrator to separate the gas from the wet oil (Fig. 33d). Several plants of this type are used in the Montana-Wyoming region where pipe-line requirements limit clean oil "cuts" to 0.5 per cent.

Fresh emulsions from a well are less resistant to dehydration than those pumped into a tank and stored before treatment. The stability of an emulsion is a function of its age. Consequently "flow-line" treating has many advantages over "batch" treating and reductions in dehydration costs have been effected by converting batch treating to flow-line treating systems. Due to the lower treating temperatures in flow-line treaters, the volume losses and gravity changes that may occur in the batch system are reduced or avoided completely. Evaporation losses are minimized as a result of eliminating wet-oil storage tanks. In flow-line treating further savings are realized ^{468a} by substantial reduction of chemical-aid requirements.

A recent development in equipment for treating emulsions is an automatic flow-line treater consisting of an oil and gas separator, a gas heater, a baffled water-wash section, and a settling space all in one unit. The treaters are operated either under pressure or at atmospheric con-

ditions. A section through one type of treater is shown in Fig. 33e. Fluids from the well enter the gas-separating chamber in the upper part of the main chamber, and the free gas is separated from the water and oil. The fluids drop down through the internal flume and enter the hot wash-water in the baffled water-wash section. The external gas heater preheats the fluid in the lower part of the flume. A gas-trap pan below the bottom baffle prevents gas from entering the wash section. The gas-vent stack conducts the trapped gases from the gas-trap pan to the separating chamber, preventing agitation and ineffective settling. The clean oil at the top of the settling space is skimmed off automatically through a discharge valve. The salt water is released to the bottom of the treater. The salt-water level is regulated by an adjustable screw on the top head of the tank.

The Petroleum Rectifying Co. of California was organized in 1911. This company confines its activities to the field of crude-oil dehydration and desalting in an effort to give to the oil industry the latest and best in electrical treating equipment.

Only in a few instances can the crude emulsions in the Talco pool be successfully treated with chemicals, because the emulsifying agent cannot be definitely determined. The "flow line" method of dehydration with electrical units has proved to be most effective in all cases. The oil is run directly from the well through the dehydrator and then into the dry-oil stock tanks.⁶⁰⁸

"Flow-line" treatment is a term that has been applied to electrical resolution of crude-petroleum emulsions by the Petreco Process. In this

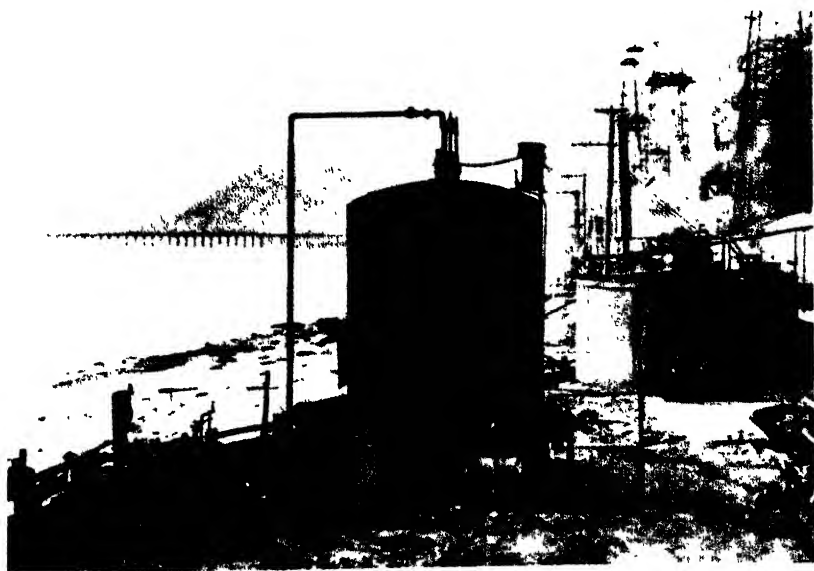


FIG. 35.

process, the emulsified oil is conducted directly and continuously from the producing well in the dehydrator, where it is treated to pipe-line requirements. (See Figs. 34, 35, and 36.)

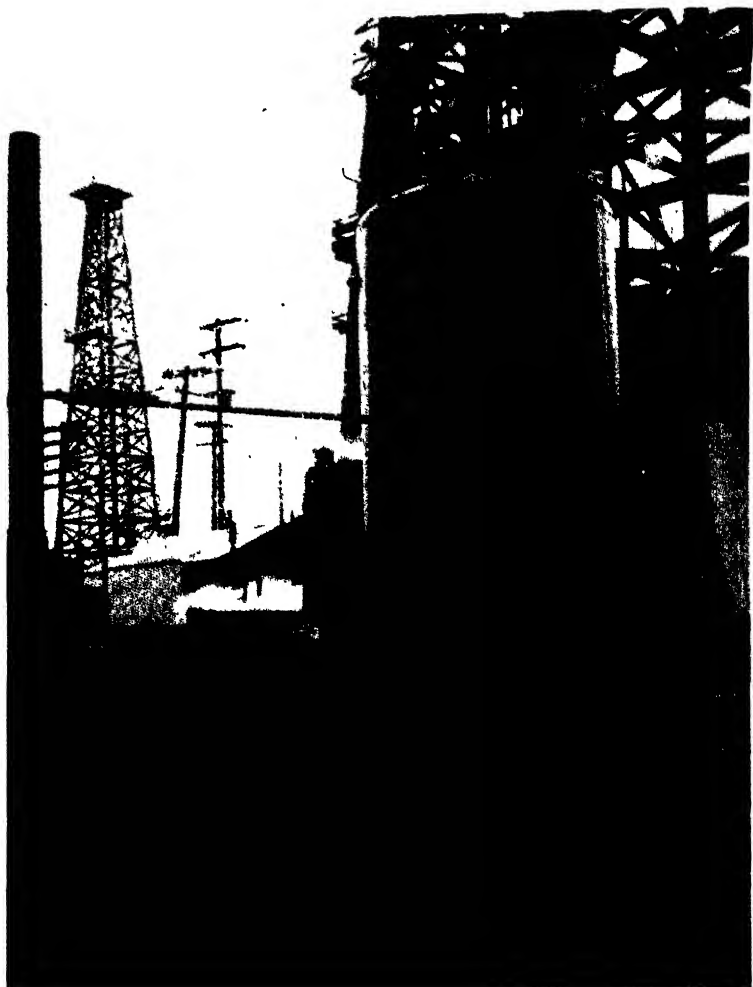


FIG. 36. Single Unit Petreco Dehydrating Plant.

Recognizing that a crude-petroleum emulsion is a system with a dynamic equilibrium and that an emulsion taken fresh from a well responds readily to treatment, it is obvious that the least possible delay in dehydration is necessary for effective dehydration. On the other hand, by conducting the emulsified oil directly from the well to the dehydrator, no stratification or sludging can occur, as the emulsion is delivered continuously to the dehydrator. No re-runs and recirculations

are necessary. The treater operating on "average" oil requires minimum supervision. Certain construction changes incorporated into the "flow-line" treaters have made them automatic in operation. Thus many factors contribute to an increased efficiency and decreased cost of dehydration by using the flow-line system of electrical dehydration.⁴³³

The principal advantage of the flow-line or Electroflow system over most of the present tank dehydrating plants lies in automatic operation: (1) an automatic control of current by means of a choke coil; (2) the automatic float-operated switch on the transformer which opens the electric circuit whenever the dehydrator is not full; and (3) the relief valve, or vent, on the dehydrator which automatically limits the pressure to a predetermined value. Fig. 37 shows the automatic control features on a

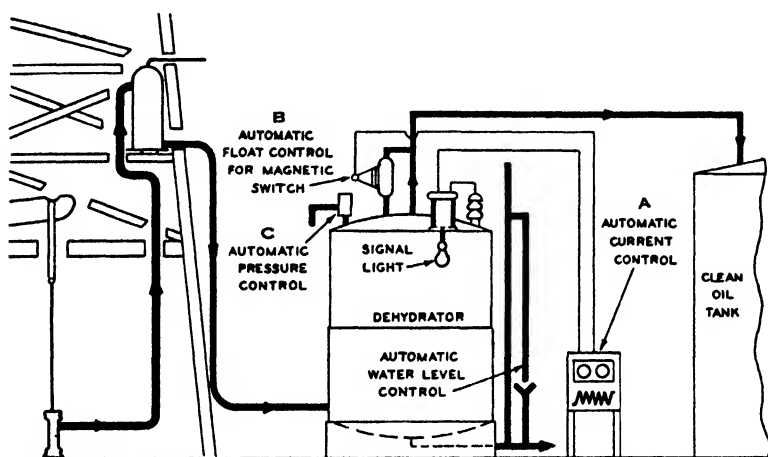


FIG. 37. Diagram of Flow-line Method of Electric Dehydration.

small unit (5 feet in diameter). *A* is the choke coil which limits the current on short circuit to 30 amperes and protects the transformer and current leads; *B* is the float control for the magnetic switch, which prevents the occurrence of arcs in the dehydrator when it is not full of oil; and *C* is the pressure relief valve, which prevents excess pressure from building up inside the dehydrator shell.⁶⁵¹ A diagrammatic sketch of a complete electric dehydrating plant equipped for automatic operation is shown in Fig. 38.

Fortine¹⁶² shows two types of electric dehydrating plants in his diagrammatic sketches. The flow-line dehydrator is controlled automatically. The process is controlled by the following features: (1) automatic control of current by a choke coil; (2) automatic float-operated switch on the primary transformer, which opens the electrical circuit when the dehydrator is not full; (3) relief valve on the dehydrator; (4) automatic flow of wet oil; (5) automatic temperature control, and (6) automatic water-level control.

The advantages of the flow-line system of electrical dehydration over the old tank system, in which the emulsion is heated by high-pressure exhaust steam, are as follows: (1) elimination of wet-oil storage tanks and dehydrator feed pumps; (2) lower operating temperature, eliminating cooling towers, etc.; (3) elimination of chemical aid; (4) no re-running of partially dehydrated oil; (5) reduction in labor; (6) elimination of gravity losses, and (7) lower plant investment cost.¹⁶²

The electric process, supplemented with some other treatment, is often encountered. A combination of electric and heat treatments is not rare. McKibben⁸³⁴ dehydrated a heavy-oil emulsion by heating it to the vaporizing point and passing the mixture continuously through an intense electric field. The vapors were condensed, the liquids cooled below the

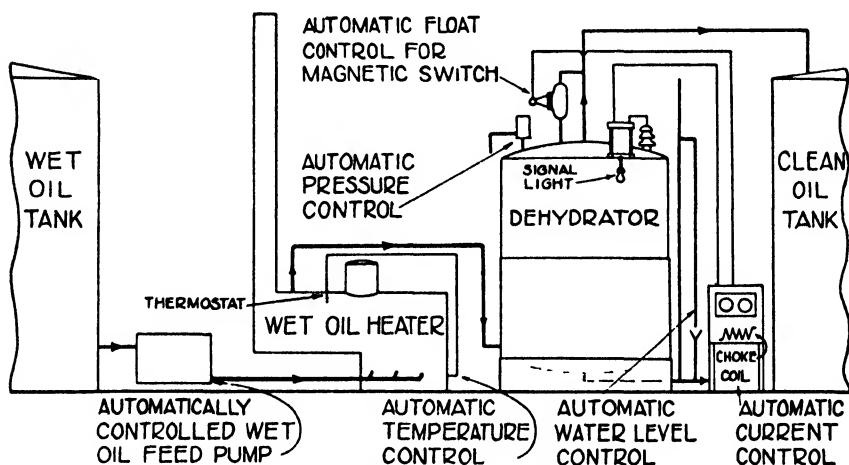


Fig. 38. Diagram of Tank Method of Electric Dehydration.

vaporizing point and the water, after settling to the bottom of the container, automatically discharged.

H. C. Eddy¹²⁵ pointed out that the highest temperature used on extremely difficult and viscous emulsions dehydrated electrically was 180° F; the average temperature is considered to be 135° F. The lower-gravity oils usually require a certain amount of heat before they can be handled or pumped satisfactorily. At the temperature required for handling low-gravity oil, emulsions ordinarily can be broken electrically and practically none of the volatile substances are lost.

Heat in conjunction with electric dehydration is applied by the Magnolia Petroleum Co.⁶⁴² Electric dehydrators operate on emulsions which have been heated to 175-190° F. For dehydration of viscous and oxidized emulsions, especially petroleum emulsions, these are mixed with a gas under pressure so that at least one part of the gas is absorbed. After removal of gases not absorbed, the emulsion is subjected to the action of a high-voltage electric field under pressure, whereby the separation of

water takes place. After the discharge of the separate phases, the gas set free is recycled to the untreated emulsion. For the treatment of petroleum emulsions natural gas containing chiefly CH_4 and C_2H_6 , likewise CO_2 , air, a mixture of CO_2 and N_2 or generator gas may be used.³⁸⁸

Passler and Brunnbauer^{375b} in resolving petroleum emulsions by an electric field, recommended that the separation of water and solid impurities should be carried out by treating the preheated emulsion with a high-tension alternating current by passing the emulsion between a multiplicity of electrodes, the conducting parts of which are insulated from the emulsion by a solid, whereby the flow of conduction current through the emulsion is prevented.

Resolution of water-tar emulsions is carried out under pressure and heating by coagulation of the aqueous phase in the electric field. The apparatus used permits producing two different electric fields.⁴⁰⁰ To resolve a petroleum emulsion, it is led under a pressure of 23-14 atms through an enlarged tube, in which an electric field of about 13,000 volts is maintained by centrally located electrodes. The gas, oil and water are separated from one another in a settling chamber connected with it. It is recommended especially to produce a foam from the gas, oil and water by introducing an inert gas under high pressure, before treatment in the electric field at lower pressures, and then to conduct the fluid into the settling chamber. The water droplets attain about the same size and may be readily separated in the settling chamber.⁴⁰⁴

The heavy, asphaltic crude oil from the Luling field is accompanied by slightly brackish water in proportions frequently as high as 98 per cent of water to 2 per cent of oil. Chemical treatment was found useless. The only successful method appeared to be heating, but neither heat exchange nor direct heating in boilers was found of any use. The new system proposed consisted of a steam-operated preheater, in which the emulsion is heated to 175-190° F and thence to a 100 h.p., 300-lb pressure boiler. The treated emulsion passes then to a battery of six electrical dehydration units of conventional type, operating at 11,500 volts. The emulsion is first settled as much as possible in the field, and then pumped into two accumulating tanks before being passed to the treating system.⁶⁴¹

When electric dehydration is carried out at higher temperatures, the effect of pressure is marked and depends on the quantity of gas and low-boiling hydrocarbons present in the crude oil. Sufficient pressure to prevent any gas being formed, in some cases, increases the treating capacity and reduces the water content of the dehydrated oil. Frequently, the normal operating pressure is sufficient to prevent gassing inside the dehydrator. This is true where the dehydrated oil passes through heat exchangers or a cooling tower before entering the stock tank. For increasing the pressure above the normal operating pressure, a spring-loaded relief valve is placed in the dehydrated oil line. This valve must hold a constant pressure, irrespective of the volume of oil passing through.⁶⁵⁰

According to a Japanese author,⁴⁵⁰ there are three methods for continuous electric purification of oil: (1) steam is blown into the oil when there is a large amount of emulsion; (2) powder is added when the oil is extremely contaminated; and (3) fibrous material is used when there is a small amount of suspension. In the first method, the oil is charged to a cylindrical metal container having a steam inlet pipe at the bottom and a bar suspended in the center, forming electrodes with the wall. The oil is externally heated to a moderate temperature and steam is blown in while a high-tension electric current is applied. Eddy currents are set up in the oil which result in coagulation and subsequent precipitation of the emulsion or suspended material. In the second method, the oil is charged with a small proportion of white clay, magnesia or titania, heated externally and stirred mechanically. An electric current causes coagulation and precipitation. It is necessary to select powders having a charge of the colloid opposite to that of the colloid to be removed. In the third method, emulsions move under the influence of electric power and adhere to fibrous materials, such as cotton, floss silk or glass wool, inserted between the electrodes. It is possible to operate it continuously and effectively.⁴⁵⁰

Kuczynski's²⁸³ findings indicate that the sign of the charge on the water globules depends only on the reaction of the water. The acidity or alkalinity of the emulsion controls the sign of the charge of "sand." De Groote,¹⁹¹ in destroying petroleum emulsions, combined filtration and electric dehydration, together with some mechanical alteration of the emulsion.

Petroleum Rectifying Co. (Cottrell^{384a}) dehydrates mineral oils under the influence of a high-voltage electric field. In this process, the oil-water emulsion is led through a coarse filter, the pores of which are larger than the water droplets; it is then brought into a treating chamber and passed from it through a fine-grained filter the pores of which are smaller than the water droplets. The electric field should act in such a manner that the water droplets tend to move in a direction opposite to that of the oil stream.

To maintain the non-conductivity of oil containing water in dispersed form, preferentially water-wettable granules such as magnetite, hematite, quartz sand, broken quartz or flintstone, or alumina, of a density 2.5, are allowed to fall through a horizontal electrostatic field at a rate faster than the flow of the oil emulsion. These granules are withdrawn from a pool of collected water at the bottom, freed from excess moisture but not rendered dry, and again showered into the apparatus.⁸²

Harris'²¹⁵ patent specifies an electric dehydration process in which solid particles, such as kieselguhr, added to the oil and water, are agglomerated about these particles by the action of an electric current. Breaking of oil-water emulsions occurs²⁰³ when these are subjected to the action of an electric field of many hundred volts, whereby the emulsion is simultaneously treated with solid-grained substances kept steadily in motion through the upward-streaming oil.

The resolution of petroleum emulsions or the like containing foreign matter is effected when an electric field is impressed on the emulsion and foreign matter in the oil is bombarded with charged particles of a liquid dissimilar to the oil and having a greater affinity for the foreign matter than for the oil, such as an aqueous electrolyte solution. The impurities of the crude oil, such as sand and sludge, charged negatively, are driven against the receiver wall, where they are taken up and led away by a liquid streaming along the receiver wall in a thin layer (the liquid wets the impurities). Outside the receiver the purified crude oil is separated from the treating liquid charged with its impurities. The inside wall surface of the receiver may be covered with a readily wetted mass, such as plaster of paris.³⁹³

In shipping oil in tank steamers the empty tanks are often filled with water; as a result, emulsions are formed with the remaining oil. To break these emulsions, a Ca or Mg soap, soluble in oil, may be used and a gas introduced, whereby separation into an oil-rich emulsion and water follows. The oil-rich emulsion is then separated from the gas and resolved by an electric field into oil and water.³⁹⁹

A continuous apparatus for separating water and solids from petroleum emulsions by electric treatment is described by Passler.³⁷⁵ Gulf Production Co.²⁰¹ formerly used a combination of heat, direct current and a centrifugal treatment. The emulsion from the field is pumped into two large, earthen storage tanks, where settling of the free water takes place. The emulsion is then heated in a closed system to 175° and sent to twelve direct-current electrical treaters, where the emulsion is reduced from 30 per cent to about 6 per cent water content. The discharge from these treaters goes to a concrete pit, where the top is skimmed to the pipe-line oil pit and the bottom pumped to eighteen centrifuge machines. The oil derived from the centrifuges has about 1.3 per cent "BS" and enters the pipe-line pit. The water from the treaters and centrifuges is handled through concrete pits and nothing but clear water is run off.

Summarizing briefly our knowledge on electric dehydration, we must consider the fact that a very high percentage of emulsions treated in California is subjected to the electric process. Even where crude oil is topped, an electric dehydrator is often installed ahead of the topping plant. One of the main features of the electric method in the dehydration process is its simplicity of operation. It is a known fact that every crude oil to be electrically demulsified must first be subjected to a test to determine its behavior in the electric field, because it is not possible to dehydrate successfully all emulsions by using electric methods, as the interfacial film in some emulsions is not susceptible to the effects of electrostatic induction. However, it must be noted that electric dehydration effects are not conditioned by the viscosity of the oil.

On the other hand, many oils are particularly suitable for the electric process. The outstanding primary advantages of electric dehydration, besides simplicity, ease of control, and centralization of operation, are: no change in the oil, high speed (*i.e.*, the large ratio of daily throughput

to volume of fluid in process), high efficiency, etc. Secondary advantages, which are not unique features of electric dehydration, are: low temperature requirements, low operating costs, etc.

Magnetic Dehydration

Magnetic separation of emulsions, although used less frequently than electric separation in dehydration, has been experimented with in a few cases. Roberts³⁹⁵ patented a process in which the emulsion is passed once through a magnetic separator. The latter is a tube surrounded by the coil of an electromagnet. The coil may be energized by either alternating or direct current. The conduit for the liquid is axial to the exciting coil. The emulsion is subjected to the action of the magnetic field, whereby the dispersed droplets are coalesced into larger masses. An advantage claimed for the process is that the emulsion is heated by electromagnetic induction. Mixed emulsions may be subjected to the action of magnetism repeatedly and at different frequencies, each frequency being adapted to one component of the mixture. The treated emulsion, after subjection to the magnetic field, is collected in a settling tank, in which separation into oil and water occurs.

Dehydration Under Action of Rays

The action of various rays has been suggested in the practice of resolving emulsions. Herbsman²³¹ patented a process of separating emulsions under the action of ionizing rays. Petroleum emulsions were subjected to the action of ultraviolet rays, x-rays, cathode rays, canal rays or α , β , and/or γ rays from radioactive substances, which cause ionization. The emulsions to be broken are streamed in a thin layer in the vicinity of the source of these rays.

Dehydration by Centrifuging

The fact that under certain conditions emulsions separate or segregate on standing is well known. This process is very slow and is caused by the force of gravity. The idea of replacing gravity subsidence by centrifugal subsidence originated in about 1850, but the first continuous centrifugal separator was invented by De Laval in 1878 and applied to the separation of cream from milk. In the centrifuge the system is placed in a tube and whirled at a high speed so that the axis of the tube lies in the plane of rotation. Under this action, heavier particles suspended in the liquid collect at the end of the tube. The coarse particles are thrown out first, and the smaller the particles the higher the velocity of centrifuging required. Van Calcar observed that a salt solution subjected to a moderate centrifugal force acquired a measurable difference in concentration between the center and the periphery. By centrifuging, about three-eighths of the salt from a saturated Glauber's salt solution could be crystallized out, and this was considered as indicating that cen-

trifugal and gravity subsidence both depend upon the difference in the specific gravity. The absolute density of the disperse phase must be great enough for separation to take place.

Stokes (1849) proposed a law expressing in a mathematical form the motion of suspended particles, pointing out the relative unimportance of the absolute density. Ayres²³ explained this contradiction by saying that Stokes' law is not applicable, in its usual form, for the size determination of highly dispersed colloidal particles, because the force of gravity is too small to produce a sufficient velocity inside the disperse phase. A centrifugal force has to be used which, at a very high speed of the centrifuge, may exceed from 15,000-18,000 times the gravity force²⁷ or 13,200 to 42,000 times the latter.²⁵⁶ Ayres suggested a modification of Stokes' formula because in a centrifuge subsidence of particles occurs not under the force of gravity but under centrifugal force. The velocity in Stokes' formula has, therefore, been replaced by the rate of displacement of particles in the direction from the axis of rotation of the centrifuge to the periphery of the chamber containing the centrifuged system, *i.e.*, dx/dt , where x is the distance of particles from the axis of rotation and t the corresponding time. The force of gravity, g , he replaced in the formula by the expression $\alpha^2 x$, in which α is the angular speed. Thus Stokes' formula takes the following form:

$$6\pi\eta r \frac{dx}{dt} = 4/3\pi r^3(D - D')\alpha^2 x; \text{ from which,}$$

$$dx/x = \frac{2r^2(D - D')\alpha^2 dt}{9\eta}$$

Ayres integrated this equation between the limits x' and x'' , and obtained

$$\ln x''/x' = \frac{2r^2(D - D')\alpha^2 t}{9\eta}$$

$$r = \frac{\sqrt{9\eta \ln x''/x'}}{2(D - D')\alpha^2 t}$$

In the case of dispersion systems having very small particles (ultra-microns less than $5 \mu\mu$ in size), subsidence with the ordinary centrifuge which develops 50,000 g or less is impossible, and the size limit for this force is indicated by Ayres to be about $3 \mu\mu$. Svedberg⁵⁰¹ constructed the first ultracentrifuge at Upsala University. It is a very complicated arrangement * because any kind of vibration, change of temperature and

* A Svedberg type of ultracentrifuge is in use at the du Pont de Nemours Company Laboratories (E. Kraemer). The world's most powerful ultracentrifuge was designed and built at the University of Virginia by Dr. J. W. Beams and co-workers and was described in *Science*, 78, 338 (1933) and *Phys. Rev.*, 39, 858 (1932). This centrifuge operates at speeds up to 20,000 revolutions per second and develops centrifugal forces from 5,000,000 to 6,000,000 times gravity.

other disturbing factors have to be excluded. The liquid investigated is placed in a special cell and hermetically sealed. Commercial supercentrifuges usually operate at 15,000 r.p.m., whereas laboratory ultracentrifuges make about 40,000 r.p.m. At such high velocities no turbulent or other effects interfere with proper sedimentation.

Centrifuging periods range between 3.5 seconds and 6.67 minutes. Sharples supercentrifuges handle 300-400 gallons per hour at a speed of about 15,000 r.p.m. As the bowl has a capacity not greater than 5 gallons, the above throughput corresponds to a total centrifuging time of 45-60 seconds. Centrifuges are in daily use in practically every oil field in the United States, where they are employed in testing crude oil to determine its BS and water content. The reasons why crude-oil emulsions are no longer treated with centrifuges in oil-field practice are broadly as follows: (1) inability to resolve stable emulsions; (2) wastage of oil in the unresolved emulsion; (3) excessive operating costs; (4) low capacity; (5) necessity for highly skilled operators; and (6) great operating hazards (fire, injuries, etc.). Centrifugal separation is usually carried out with two types of centrifuge: (1) the continuous, and (2) the batch. The relative specific gravities of the components in the centrifuged system determine their direction of motion. In the one, a container is filled with the liquid and rotated, if the particles have higher specific gravities than the liquid. They move until they are held firmly at the bottom of the container before any separation can be measured. In the other, the liquid is passed continuously through a rotating cylinder and drawn off from a point near the center of rotation. While the centrifuge is still in motion, a separation can be seen, according to Ayres,²⁰ when the particles have moved only a fraction of the distance to the bottom. The continuous centrifuge is considered to be the more useful type. The superiority of the continuous centrifuge is based on the possibility of handling larger volumes of liquids. When the volume is large, the liquid must pass rapidly through the rotor, and the time of action of the centrifugal force upon the disperse phase must be limited. Ayres considers that the time is dependent upon the stationary capacity of the rotor, and that the size of particles that can be removed within a definite time is limited. The time required for each particle of a given dispersoid to move from its position in a uniform distribution to its equilibrium position is constant.²⁰

In studying the principles underlying the law of distribution, Ayres found the concentration to be greatest at the bottom and to vary in an exponential manner with the height, according to Perrin's law, expressed by the equation:

$$\log_e C_0/C_x = mgKx,$$

where C_0 is the concentration of particles at the initial level O ; C_x , at the height x ; m , the mass of the particle; g , the acceleration of gravity, and K , a constant. The centrifugal force fxg at any point, x , is a function of x involving the centrifugal force at the periphery. The general

expression for distribution of particles in case of centrifugal force has been formulated by Ayres as follows:

$$\log_e C_0/C_s = mfgkx.$$

The highest commercial centrifugal force applied is 50,000 times gravity.²⁰

As stated by Ayres, the determining factors of the centrifuging process are: (1) not too high a viscosity of the continuous phase, otherwise the subsidence is too slow; (2) a certain minimum size of particles determined by the viscosity; and (3) the gravity differential between the dispersoid and the dispersing medium.

A poly-disperse system, containing particles of several degrees of dispersion, can be accurately fractionated with various degrees of centrifugal force. Ayres actually succeeded in showing that if a separation is impossible with a lower force even over a long period of time, it can be secured in a very short time by a more powerful machine. An emulsion of crude oil containing 9 per cent of water, when diluted with gasoline and subjected to a force of 1700 times gravity, gave 0.9 per cent water separation within 30 minutes. The percentage recovery was not increased by extending the time to five hours. When the same mixture was passed through a high-power centrifuge at a rate equivalent to less than one minute for separation, the yield of water was 8.8 per cent.

Ayres²³ pointed out an interesting fact that the highest centrifugal force causes no greater degree of coalescence than gravity alone. He also noted that the small globules in a settled emulsion are packed by gravity into a space as small as they can be packed by the highest centrifugal force. Stable emulsions can only be sludged, not broken, by centrifuging. Many emulsions cannot be concentrated by gravity to contain more than 30 per cent of the disperse phase. Concentrated crude-petroleum emulsions rarely contain more than 55 per cent of water. The size of globules ranges from less than 0.5μ to 50μ or more in petroleum emulsions. Photomicrographs show that great heterogeneity is the rule, rather than the exception, and is unrelated to the concentration of the disperse phase.

On the other hand, much more stable emulsions can be concentrated by centrifugal subsidence up to 80 per cent of the disperse phase. The advantage of the centrifuge over the action of gravity is pointed out by Ayres as follows: if, for example, the centrifugal force is 15,000 to 18,000 times the force of gravity, separation by gravity will take 15,000 to 18,000 times as long as by the centrifugal force. Kansas, Oklahoma and some Texas emulsions require the exertion of a centrifugal force of this magnitude to effect subsidence in a one-inch emulsion layer during a period of from 6 to 18 seconds, while for the force of gravity the time element is from 24 hours to 3 days. Ayres determined also that when conditions are such that a particle does not settle completely by gravity, centrifugal force will cause complete subsidence only in case the product of the mass in grams, the force in dynes and the constant 3×10^{-16} is greater than or equal to 10. When the product is less than 10, only

partial subsidence takes place. A force of 50,000 times gravity can completely remove particles as small as $3\ \mu\mu$, the separation requiring 30 hours; but this limiting particle size is likewise a joint function of the gravity differential and the viscosity of the dispersing medium ($d = 0.1$; $\eta = 0.01$).

Sometimes the centrifuging is too slow, resulting in incompletely separated emulsions. Heat is of importance to centrifugal separation in that it decreases the viscosity of the oil, and also changes the gravity differential. In some cases, heating an emulsion may induce coalescence, and may thus be a method for decreasing the stability of the stabilizing film at the interface. It is advisable, therefore, that the more stable emulsions be centrifuged at high temperature in order to decrease the time required for complete subsidence.

A complete resolution is accomplished by proper heating of the emulsion or by centrifuging first at normal temperature, heating the concentrated emulsion to effect coalescence, and then re-centrifuging. When large amounts of inorganic substances are present in the crude oil they must be removed from the emulsion before centrifugal separation can be carried out, and this involves heating, settling and treating with chemicals, followed by centrifuging. Crudes of very high viscosity cannot be dehydrated economically by centrifuging. The number of recommended reagents to be used in connection with centrifugal treatment is very large.²⁴ Soluble colloids, ordinary soap, resin and naphtha soaps, starch, glue, albumin, casein and sodium resin soap have proved to be most effective in the case of water-in-oil emulsions.

The continuous centrifuge is considered superior to the non-continuous type, particularly with reference to handling liquids in commercial quantities. In this case the highest centrifugal force applied was 40,000 times gravity, and the maximum time for the lowest practical rate of continuous flow was found to be about 20 minutes. One per cent suspensions of particles of various densities in liquids of various viscosities have been completely separated by the use of a continuous centrifuge according to the following table:

Table 4

Size of Particle		Viscosity
$d = 1.00$	$1.00\ \mu\mu$.0001
	$3.0\ \mu\mu$.001
	$10.0\ \mu\mu$.01
	$30.0\ \mu\mu$.10
	$0.1\ \mu$	1.00
	$0.3\ \mu$	10.00
$d = 0.01$	$10.0\ \mu\mu$.0001
	$30.0\ \mu\mu$.001
	$0.1\ \mu$.01
	$0.3\ \mu$.10
	$1.0\ \mu$	1.00
	$3.0\ \mu$	10.00

When the volume is great, the liquid must pass through the rotor quickly, for the time during which the centrifugal force can act on the dispersoid

is limited (the time in each case is dependent upon the stationary capacity of the rotor). For instance, if 10 liters of a liquid flow through a rotor before the level is high enough to overflow or discharge, it is apparent that the time in minutes during which each unit of liquid remains in the rotor will be equal to the rate of flow in liters per minute divided by 10. However, the actual time is less than the quotient obtained by an interval, depending on the mechanical arrangement of feeding, the amount discharged, etc. The capacity of a high-speed centrifugal rotor is limited in practice by the strength of the material to be centrifuged, but the degree of centrifugal force exerted has not yet reached any such practical limit.²³

De Laval separators do not find ready application in the petroleum industry. The Sharples supercentrifuge is another separator used in dehydration practice by centrifugal treatment. The advantage of this machine over the ordinary type lies in the increased speed, as well as in a special construction of the rotor, which increases the time during which the centrifugal force acts upon the material under treatment. The supercentrifuge operates on the principle of the cream separator and consists of a small elongated cylindrical bowl, capable of being rotated at 18,000 revolutions per minute. This bowl has a diameter of 4.5 in, is 30 in long, weighs 35 lbs, and is driven by a turbine or motor, through a vertical shaft or spindle. Inside the bowl is a three-winged vane, which prevents losing some of the centrifugal effect caused by slipping of the liquid relative to the bowl. Broadbent⁶⁶ described a type of steam-driven, bottom-discharge centrifuge and an electrically driven centrifuge for separating liquids of different specific gravities. de Kadt²⁶¹ stated that Mexican raw oil emulsions with 50 per cent or more of water may be cleaned within 30 to 50 minutes at 35,000 to 40,000 revolutions per minute in a supercentrifuge.

According to Killeffer,²⁶⁹ centrifuges are used for the separation of oil and gas. The separation of water from gas-tar emulsions by centrifuging is reported by Hauschildt.²¹⁹ Prater considers the separation of water from gas-tar emulsions (from coal-tar distillation) more difficult than from illuminating gas-tar emulsions. Prater used a Sharples supercentrifuge which resolved the emulsion into tar, water, and a layer which remained in the centrifuge, while the tar and water flowed out separately. The emulsion containing about 46 per cent of water enters the centrifuge at 80° F. The dehydrated tar does not contain more than 1.25 per cent of water. The reason for the formation of an emulsion was assumed to be due to the highly polymerized tarry or resinous material; the centrifuged tar and water alone do not form stable emulsions. However, Roberts reports that his experience with gas-tar emulsions indicates that centrifugally resolved tar emulsifies quite easily with water. Sharples Specialty Co.⁴⁶³ claim a centrifuging method, comprising three or more phases, for the resolution of complex emulsions. In this process, separation is effected with discharge of the intermediate phase, including the

heaviest, and recovery of substantially all the lightest part. The stability of the emulsion comprising the intermediate phase is reduced and its resolution produced by centrifugal subsidence.

Sharples Specialty Co.,⁴⁶⁵ in order to break a petroleum water-in-oil emulsion, adds about one per cent of a mixture of sodium resinate, resin and water, and then centrifuges. In the case of an oil-in-water emulsion, a solution of calcium oleate, in equal parts of alcohol and glycerin, is used, to which about 0.5 per cent of gelatin is added; the solution is then centrifuged. Sharples Specialty Co.⁴⁶⁶ patented still another dehydration process in which the mixture entered a decantation chamber and settled by gravity, passed into a separator and the output was led into a centrifuge. The material floating over in the decantation chamber is united with that obtained after centrifuging. Wright,⁶⁵⁵ when dehydrating an oil, atomizes it with a stream of hot water against a rotating, inclined plate. The oil is separated from the impurities by centrifuging. Empson¹⁴⁵ used a centrifuge so constructed that the emulsion is first treated in the zone of maximum centrifugal force, whereby the coarse impurities and a certain portion of the water is precipitated, and the emulsion passed through a filter composed of a layer of sheets of paper or other suitable material, in order to separate the colloidal and other suspended substances.

Haynes, Marx and Rozies²²⁰ developed a method for the purification of oils containing suspended colloidal substances, whereby centrifuging and electrical precipitation were combined in one apparatus called the electro-centrifugal separator. By treating this oil for five minutes with an electric field having a strength of 40,000 volts and centrifuging the liquid at a speed of 2700 r.p.m., they succeeded in obtaining an optically pure oil. Westinghouse Co.⁶³¹ used a special centrifuge chamber for the dehydration of oils. Green and Ogden¹⁸⁷ patented a centrifugal separator especially suitable for liquids with little difference in their specific gravities. Aktiebolaget¹¹ constructed a centrifugal separator similar to the Sharples centrifuge. The German centrifuge of Heine Viersen Bros. and the Triumphator centrifuge are also similar to that of Sharples.

In the Breckenridge field, where a high-gravity paraffin-base oil was produced, the resulting emulsion was subjected to centrifugal treatment. A capacity of 250 barrels per 24 hours was easily maintained. In the Kansas fields and some parts of Oklahoma where a different type of emulsion was found, the production was as low as 50 barrels per day. Complete dehydration has been claimed in the case of emulsions from the Osage district. At present, not a single centrifuge is used in any oil field of the United States for the purpose of treating crude-oil emulsions. The last centrifuge used as an oil-field crude-oil dehydrating device was abandoned at Robberson, Oklahoma in 1926. The current use of centrifuges is in refining practice. Supercentrifuges are used for deparaffination and the production of vaseline, as well as in the refining of used lubricating oils and for similar purposes.

REFINING PROCESSES AND METHODS OF PREVENTING
AND RESOLVING EMULSIONS

In certain processes for the refining of crude petroleum, there exist conditions which assist in the formation of emulsions; in other refining processes continuous emulsification is prevented. Insofar as refining processes are often accompanied by emulsion formation, it is important to choose correct methods for the refining of petroleum distillates in order to avoid their formation. The breaking of emulsions formed during the refining process may sometimes cause more trouble than the refining process itself. There are several reasons for the formation of emulsions when treating petroleum products. Most frequently the formation of emulsions is related to compounds produced when washing with alkali. These substances include complex compounds of sulfuric acid, such as sulfonic compounds and naphthenic acids. These combine with sodium, magnesium and calcium, forming soaps which assist emulsion formation. Strong alkaline solutions for refining are to be avoided, for soaps soluble in oil may be readily salted out.

Refining is best carried out at low temperatures, using strong alkalis, but the tendency toward emulsion formation suggests the contrary. Neutralizing the refined distillate with alkali, as well as washing it with water, causes emulsion formation. Vigorous mixing or stirring during neutralizing or washing should be avoided because of emulsion formation. Distillates treated with fuming sulfuric acid, when subjected to further refining, show a strong tendency toward emulsification. Overtreatment with sulfuric acid, either by addition of excessive quantities of acid or too rapid addition of the acid, too vigorous agitation, or improper temperatures, may be responsible to a great extent for the emulsification of stocks that have been acid-treated. Straight-run gasoline and some kerosene will emulsify because of the formation of a soap, resulting from a combination of mineral elements in the wash water and the derivatives of sulfur or naphthenic bodies naturally present in the oil and formed by the reaction. Gruse,²⁰⁰ in his book, states that relatively high temperatures, just below the initial boiling point, during treating and alkali washing, are considered good practice. In all probability certain of the sulfonic acids formed during the acid treatment, which are excellent emulsifiers, are decomposed at this temperature.

Refining processes may be divided into the following classes: (1) refining with acids, sulfuric acid being principally used; (2) refining with alkalis (sometimes heat and pressure are used additionally); (3) refining with various salts, as well as organic liquids; (4) refining by the oxidation of crude products, using oxygen obtained from the air; and (5) refining by the use of various adsorbents, which process finds the largest application.

The action of sulfuric acid on petroleum may be utilized in refining, and particularly in separating large amounts of resins and tars. Gurwitsch²⁰⁸ found that sulfuric acid reacts with a resin, forming a very

labile compound which splits off acids on standing. The addition of 5-per cent sulfuric acid at room temperature is sufficient to refine petroleum. On the other hand, a considerable part of the petroleum is thus polymerized. This polymerization occurs at the expense of the unsaturated hydrocarbons⁶⁵⁸ which partially dissolve in the sulfuric acid. The high-boiling fractions (300°) of petroleum are almost always adsorbed by sulfuric acid. But, in spite of the removal of these high-boiling fractions, petroleum treated with sulfuric acid is not essentially richer in low-boiling hydrocarbons as compared with crude petroleum. Zalozet-sky⁶⁵⁸ explains this fact by the formation of polymerized hydrocarbons of a high boiling point. The refining of petroleum with sulfuric acid has a good effect on lubricating oil distillates. Because of polymerization, the lighter lubricating oil distillates are converted into the heavier distillates, acquiring a higher viscosity and separating in a purer state than from the crude petroleum. If heat and pressure are applied in the treatment of petroleum in sealed tubes, changes occur in the petroleum. Petroleum distilled at 300°, when compared with petroleum not distilled, shows a decrease in the ingredients adsorbed by sulfuric acid, whereas the formation of unsaturated products would be expected, as well as an increase in soluble ingredients. The fact that products become insoluble indicates that the hydrocarbons are polymerized or isomerized by heat and pressure, and this causes them to become non-reactive with and insoluble in sulfuric acid. Saturated hydrocarbons not of the paraffin series are converted into unsaturated hydrocarbons, and naphthenes into olefins. On the other hand, another type of isomerism between naphthenes and olefins may be expected, namely, the so-called dynamic isomerism set forth by Berthelot.⁵⁰

In the case of sulfuric acid treatment, the entrance of the sulfo- group into the molecule must be taken into consideration, sulfo-acids being formed. According to Gurwitsch,²⁰⁹ sulfo-acids, in contrast to naphthenic and fatty acids, are soluble in water not only in the form of alkali salts, but also as the free acids; their solutions appear to be of a colloidal character and may be readily salted out from aqueous solutions. Acid petroleum distillates cannot be emulsified with alkali solutions, but they can be emulsified with pure water, and much more readily the larger the amount of sulfo-acids formed during refining. Distillates treated with fuming sulfuric acid show a strong tendency toward emulsion formation.

Veith⁶¹³ states that petroleum, after refining, shows a certain turbidity due to the presence of organic salts and sulfo-acids formed during refining with sulfuric acid. He also indicates that this turbidity may be eliminated by treating the refined oil afterward with alkali. Because of an increase in the formation of sulfo-acids, the refining of distillates readily results in emulsified hydrocarbons. Koetschau²⁷² believes that Roumanian oils are difficult to refine because they contain both aliphatic and aromatic hydrocarbons.

Demant¹⁰⁷ refines hydrocarbons by treating them with sulfuric acid of such concentration and at such temperature that sulfonation of the

hydrocarbons does not occur; the polymerized products which are insoluble in the acid remain dissolved in the hydrocarbons. Naphtha, the solvent used, is refined with sulfuric acid (46-48° Bé) at 110° for a few hours, and the acid is drawn off from the solution; the naphtha is neutralized and then distilled with steam; phosphoric acid may be substituted for sulfuric acid. Edeleanu¹³⁴ claims that liquefied sulfurous anhydride may also be used in refining petroleum. Dunstan^{120a} suggested refining mineral oils by treating them with chlorine in the presence of water, washing with an alkaline solution, and distilling until the distillate has a density of 0.720. Smith⁴⁷⁹ patented a method for refining petroleum containing sulfur. This method consists in heating petroleum to its boiling point with a substance of the terpene series, after which the mixture is cooled and further subjected to refining with sulfuric acid.

Nastjukow³⁵⁸ discovered quite an interesting reaction between sulfuric acid and petroleum when formalin is added. When sulfuric acid and formalin are added in the volume ratio of 1:1:1/2 to the refined petroleum, an energetic reaction takes place, with the formation of a solid product, phenylformol, or "formolite." This is a yellow-brown, amorphous compound, insoluble in the ordinary solvents. The amount of formolite formed increases with an increase in the boiling point of the distillate. Different types of petroleum produce definite amounts of formolite: Russian naphtha, 5-38%; Teaghane, 17-18%; Ssurachan, 5%; Grozny, 23-24%, and Bibi-Eibat, 37-38%.

Very often alkali treatment is not a refining treatment in itself, but a second step in refining with acids. Wischin,⁶⁴⁵ at the end of the acidifying process, treats the product with one per cent of 30° Bé sodium hydroxide. The writer points out that this kind of treatment is suitable only for Russian distillates and does not approve it for Galician, Hungarian and Roumanian oils. Treatment with alkali finds application in removing odors from petroleum, as well as from its distillation products. Weber⁶²⁸ admixes pungent ethereal oils, such as turpentine, citron, lavender and pine and agitates them with sodium hydroxide while heating. Substances emitting unpleasant odors are considered to be unsaturated hydrocarbons having properties similar to those of dicyclopentadiene. These hydrocarbons, together with the terpenes, are condensed by means of alkali, rendering them non-odoriferous; they are precipitated out or remain dissolved in the benzene, with the odor of the ethereal oils predominating. Stelzer⁵⁰⁰ claims that ethereal oils used in refining petroleum have the property of adsorbing oxygen from the air and of conveying it to the impurities contained in the petroleum, rendering them resinous. The resins so formed are treated with sodium hydroxide or concentrated sulfuric acid, and then removed.

In the Nizhny-Novgorod refinery the crude oil is subjected to a preliminary caustic treatment. A saving of 42 per cent of acid, 75 per cent of caustic and 55-65 per cent of refined products is thereby obtained. The procedure is as follows: the oil is passed through fuel-oil heat exchangers and towers heated with steam coils up to 65-70°; then it is

passed through a pipe having inlets for a dilute NaOH solution, which is injected into the pipe and accompanies the crude oil during its passage through a section of the pipe. The crude oil and dilute caustic are received in a heated settler, and the oil is passed directly into the Borrmann stills, while the dilute NaOH is brought up to 4-5° Bé NaOH and used again. Because of the presence of saponified petroleum fractions in the water, emulsions were not formed. The consumption of NaOH amounted to 0.266 per cent and the loss in oil was 2.42 per cent. The refined products are claimed to be of a higher grade than those obtained in the usual procedure.²⁰⁰

An apparatus to be used for refining hydrocarbon oils, either with acids or alkalis, has been described by Skinner.⁴⁷⁷ Into a series of receivers under pressure and connected with each other by tubes, sulfuric acid is led in a direction opposite to that of the oil, both of which are mixed by a stirring arrangement. The acid is washed out by a flow of water and the oil is treated with alkali. The treatment with strong sulfuric acid is favorable in removing, through coagulation by agitation, the colloidal asphaltic matter contained in the crude oils, as well as the yellow coloring matter in benzene, kerosene, and other distillates, which is caused by a tar fog mechanically carried over.

Rütgerswerke A.-G.⁴⁴⁸ utilizes organic bases soluble in water, such as the salts of pyridine or the homologs of the primary, secondary, or tertiary amines of the aromatic series, to refine tar and tar oils. Two layers are formed, one of which contains the neutral oil and the other the salt and the phenols. Bidrewicz⁵¹ uses alcohol in refining petroleum distillates to avoid the formation of emulsions during the refining of Baku Solar oils. The treatment with alcohol follows the addition of sulfuric acid. The oil is refined with sulfuric acid, heated to 50°, mixed with 0.25-0.30 per cent alcohol, agitated for one hour and allowed to stand. Sulfo-acids are then drawn off and the oil is washed. Solar oils give about 7 per cent of sulfo-acids which possess emulsifying properties in alkali, as well as in acid and neutral aqueous solutions (hard water). In this sense they are equivalent to fatty acid soaps.

Hütz²⁵¹ refines petroleum hydrocarbons by heating them slowly up to about 230°, and distilling off the solvents with alkali metals in the presence of organic substances containing oxygen, neutral solutions such as alcohols, acetone, aldehydes, or treating directly with these alkali compounds. After cooling, air is blown through and the oil is separated from the precipitated impurities, by decantation or filtration. According to Schwarz,⁴⁵⁶ crude petroleum may be refined with salts of organic or inorganic acids, as well as with phenolates either in solid form, or as solutions in such concentration that impurities precipitate and separate; simultaneous application of acids such as naphthenic acids, which form salts or soaps with these bases, is also effective. The oil so treated does not undergo any changes and the impurities are removed. Soap-like substances, as well as large amounts of alkali, can also be used; a refined oil free from soap is formed. Hinrichs²⁴² recommends treating crude oil

with a liquid fatty acid dissolved in carbon tetrachloride, to free it from foreign substances; the mixture is warmed and allowed to stand until separation is effected.

Petroleum and its distillates are also refined with electrolytes. Mony³⁴⁹ distills petroleum hydrocarbons with small amounts of acetic acid, hydrochloric acid, or ferric sulfate, as well as potassium hydroxide and sodium hydroxide. Petroleum distillates, such as kerosene, are slowly distilled, with the addition of such substances as ferrous sulfide, antimony trisulfide, potassium carbonate, sodium carbonate, or calcium chloride, which facilitate their cracking.³⁴⁹ If necessary, the distillation is repeated with the addition of antimony chloride, potassium tartrate, or potassium carbonate. McClave³⁵⁰ mixes crude petroleum with manganese dioxide and potassium chloride, and after stirring the mixture a little, allows it to stand for from one to two days. The impurities settle to the bottom.

Petrow⁴⁰⁵ purifies petroleum by oxidizing the crude products with oxygen from the air and then treating with 65-70-per cent sulfuric acid, using heat and pressure to separate the unsaturated hydrocarbons in the form of polymerized products. Highly viscous oils are converted into non-viscous oils by refining. Brownlee and de Ganahl⁶⁷ heat oils by leading them through a series of kettles or rotating retorts. The vapors formed are withdrawn from each blast and condensed separately. Heating is best conducted under 3 to 5 atmospheres' pressure. Refining is sometimes carried out successfully by allowing the oil to flow in thin layers over heated metallic tubes to remove the water and volatile substances which it contains.^{483a}

Société Anonyme des Pétroles⁴⁸⁴ patented a method and built an apparatus for cracking heavy oils. The oil is heated by means of electric heaters arranged in parabolic reflectors. Simultaneous heating, distillation and refining of the products distilled is thus made possible. Condensation of the distilled products is made under pressure, as well as under ordinary atmospheric pressure. In order to separate petroleum from lubricating oils, Riolland⁴³⁰ atomizes the heated mixture into a gas or the vapor of a liquid not miscible with any ingredients of the mixture, then passes it into a tube with many subdivisions or zones in which the temperature decreases stepwise, where the single fractions settle out; the last zone is cooled with a spray of cold water.

Adsorption on specific adsorbent surfaces plays an important part in the refining of various distillates. For refining purposes, various earths and minerals, such as fuller's earth, china clay, alumina, magnesite, iron oxide; alkaline-earth oxides, such as calcium and magnesium, bentonite, silica gel, and bone ash; and carbonaceous materials, such as coke, coal, charcoals of various origins, bone black, and blood charcoal have been used. Adsorbents are more or less highly specific in their action and hence must be chosen with due regard to the material to be adsorbed. What actually occurs by an adsorption refining of petroleum is decolorizing, desulfurizing, and separation of unsaturated hydrocarbons. Fuller's

earth, for instance, as proved experimentally by Gilpin and Schneeberger,¹⁸¹ allows paraffins and saturated hydrocarbons to pass through freely, adsorbing bitumens, aromatic hydrocarbons, sulfur and nitrogen compounds.

Herr²³³ made an interesting observation by filtering Baku oil through fuller's earth. He found that the unsaturated compounds reacting with formolin (formolite-forming compounds) were adsorbed on the mineral gel and could not be recovered unchanged. The close contact afforded in the adsorbed layer promotes condensation and polymerization processes. That adsorption can be accompanied by purely chemical processes, such as polymerization of unsaturated compounds, has been pointed out by Gurwitsch.²⁰⁴ For example, amylene can be changed to dipentenes and other compounds by the action of hydro-silicates. Fuller's earth and charcoal act similarly. Hexylene was found to behave in the same way. Gurwitsch²⁰⁶ was able to show that Floridin produces active polymerization when brought into contact with pinene, resulting in a considerable increase in temperature. After the adsorption, pinene is converted into sesqui- and polyterpenes. Gurwitsch²⁰⁵ also showed that Floridin adsorbs solid paraffin from solution in petroleum spirit and benzine, but not from lubricating oil. Again the specific action of an adsorbent is emphasized.

Floridin also has a desulfurizing action on benzine, but has little effect on the sulfur compounds occurring in lubricating oils derived from the same crude petroleum. The adsorption capacity of Floridin finds application in removing highly unsaturated hydrocarbons, such as olefins and diolefins, with their characteristic odor. Since they tend to resinify, the diolefins subjected to the adsorption conditions of the refining operation carried out with spirit in a vapor state are polymerized to high-boiling products, setting free the spirit.

Kambara earth,⁸⁶ a mineral containing hydrated silica, is also an effective adsorption material. It decolorizes crude petroleum and adsorbs unsaturated hydrocarbons therefrom. Gowalowsky¹⁸⁴ recommended fibrous alumina as an adsorbent. The freshly ignited, precipitated alumina is particularly effective as a decolorizing agent for petroleum and its distillates. Hydrated silica or alumina is effective after the combined water has been driven off, but it is not generally so. Concerning the relationship between the chemical composition of the material and its adsorption properties, little is known. Bodies of dissimilar chemical composition may act equally effectively as decolorizing agents. The determining factors in adsorption effectiveness are extent of the surface, degree of fineness of the adsorbent and composition of the material. The temperature at which the adsorbing surface exerts its specific action should also be considered.

Gilpin and Schneeberger¹⁸¹ state that on passing California crude oil through fuller's earth, a small fractionation effect was noticed at 20°, and a much better result was obtained at 70°. Bauxite, gently agitated with kerosene or benzene, shows a very characteristic behavior, as described by Bancroft.³¹ A process of peptization takes place, for a

considerable amount of material in a fine suspension is dispersed in the petroleum. The suspension is fine enough to pass readily through a filter paper. The activity of bauxite, as stated by Dunstan,¹²⁰ is a function of temperature. Bauxite which has been ignited and cooled in a vacuum desiccator loses its power to adsorb sulfur derivatives from kerosene. When freshly ignited, bauxite possesses a powerful adsorptive action, in accordance with the "exponential" adsorption equation $a = \alpha C^{1/n}$, where a is the adsorbed amount expressed in milli-mols per gram; α and n are constants; and C is the concentration of the solution in mols per liter. The lost activity may be regained by heating to 200°. Heat also appears to be evolved by the adsorption process. Thus a 20° increase in temperature was observed by passage of 100 cc of kerosene through 50 g of bauxite.

Knowing²⁷¹ refined petroleum by filtration through activated carbon mixed with silica gel. Cross^{97a} washes the material to be refined with sulfuric acid, with cooling, and then subjects it to the action of an adsorbent, such as a highly active gel, containing substances which react with the sulfur. Elsenbast and Horine¹⁴⁴ state that there are three kinds of diatomaceous silica which may be used in refining processes: (1) one containing 89 per cent SiO_2 and 5 per cent moisture; (2) a so-called "standard silocel"; and (3) hyflo-supercel, which is practically dry and contains about 95 per cent SiO_2 . These products, admixed with the oil to be refined, remove turbidity, salts, paraffins and moisture when filtered through a cloth.

Meyer³⁴³ reports a "Miller" silica gel prepared by taking molecular proportions of water glass and sulfuric acid, mixing together and washing; a hard, glass-like product, similar in appearance to quartz and silica, is obtained. This product is porous, the pores being distributed uniformly and occupying 41 per cent of the total volume. The selective adsorption of this product lies in its ability to adsorb sulfur compounds from petroleum. The gel, saturated with impurities adsorbed during refining, can be reclaimed by heating or roasting.

There are a number of refining patents which disclose the use of molten metals.^{185a, 54a} A decomposition catalyst, such as an alloy of tin containing less than 10 per cent of antimony, has been described by Hesse.²³⁸ The hydrocarbons to be refined are allowed to flow toward an oncoming current of gas under pressure, resulting in the formation of a thick oil mist which is led through the melted catalyst.

Separation of the salts present in crude-oil emulsions is important, because they cause corrosion of equipment, plug and cause overheating of tubes, and unfavorably affect refining operations and refined products. For the analytical extraction of salts the separatory funnel methods may be used; these are based on the use of solvents alone or both solvents and demulsifying agents. As solvent acetone and sometimes benzene are used. Solvents are chosen to decrease the viscosity of the oil, increase the gravity differential between the phases, and to counteract the effect of emulsifying agents. The use of small amounts of suitable demulsifying

agents is recommended to secure more complete separation of phases, to cause destabilization of the interfaces of particles of dispersed salts, and to prevent permanent emulsification of the particles of the aqueous extract, so that subsequent settling yields a clean oil/water interface. The chemical is added either before or after the water. The oil is mixed with benzene or xylene containing the demulsifier and the mixture is vigorously shaken with water. The use of xylene is preferred to that of benzene on account of its higher boiling point, lower specific gravity, and better solvent power for most hydrocarbons. The centrifuge method is superior to simple settling methods because evaporation, volume losses, etc. are avoided, but the chief disadvantage is its expensive equipment. If only a solvent is used, then, before centrifuging, the oil, the solvent benzene and hot distilled water are mixed and vigorously agitated. The demulsifying agent is either mixed directly with the oil to destabilize the emulsion present, or added with diluents and water. The mixture is transferred to centrifuge tubes, the emulsifier rinsed with acetone and added to the tubes. For removing the water after centrifuging, a separatory funnel is used: or the water is pipetted off from the tubes and the tubes recentrifuged.^{43a}

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Chapter 4

Practical Knowledge of Emulsions

ASPHALT AND BITUMEN EMULSIONS

Introduction

Hydrocarbon emulsions have broad application, asphalt or bitumen emulsions and lubricating oil emulsions being those of greatest interest. Although used principally for road building, asphalt emulsions are extensively used in making paints, in water-proofing paper, in concrete, etc.

The paving uses of asphalt in the United States are as follows: (1) as priming and bonding coats in resurfacing; (2) in macadamization; (3) for bituminous and gravel roads; and (4) for cold patching and maintenance work. In other countries, particularly European, asphalt is used principally for highway construction and maintenance. There are three principal methods of use of asphalt and asphalt emulsions; (1) the surface method; (2) the penetration method; and (3) the mixing method. For resurfacing, either the mixing or the penetration method is the most acceptable. Emulsified asphalts were originally applied for laying dust on highways.

In applying asphalt emulsions to paint purposes, the character of films formed by spreading these emulsions must be considered. Films of emulsions of the water-in-oil type containing but little protective colloid, and characterized microscopically by the absence of any net-like or cellular structure, display a resistance to water comparable with that of oil films, since films containing much water-soluble colloid, or of the oil-in-water type, become cloudy or disintegrate completely.⁶⁰

Aside from road work, the use of bitumen or asphaltic emulsions serves other purposes, such as roofing, damp-proofing, water-proofing, paint, pipe coatings, plastics, mastics, anti-corrosives. The asphalt may be used alone or in combination with pigments, fillers, fibers and other organic and inorganic substances.

Any type of roof may be treated with an asphalt emulsion by means of a spray, brush or squeegee. All tiny cracks will be filled, all porous materials will be saturated and an impervious film of asphalt will spread over the surface. Built-up roofs may also be made, and the fluidity of the emulsion does away with the fire hazard and the equipment needed to apply hot bituminous substances.

Asphalt emulsions, instead of water, may be used in gaging cement; an increase in the setting time and only a 0.4 per cent decrease of strength are brought about. When the gaging solution is made by diluting asphalt

emulsion with 15 volumes of water, the effect of preventing the penetration of water at 1 atm pressure is sufficiently great. By diluting the emulsion with 20 volumes, the penetration of water is entirely prevented under 2 atm pressure, and for a considerable length of time even under 4 atm pressure.²⁵²

Whether or not a crude oil is suitable for preparing asphalt depends wholly on its chemical composition, and particularly on its asphaltic content. Asphaltic hydrocarbons either exist as such, or are obtained through polymerization, condensation, sulfonation, or oxidation. Abraham¹ classifies crude oils from Texas, Louisiana, California, Mexico, Venezuela, Trinidad, Colombia, Peru, Argentina, Sakhalin, Kurakawe and Niitzu as "asphalt-base" oils. Saturated hydrocarbons which are not readily polymerized are unsuitable for direct production of asphalt; however, by the action of high temperatures and high pressures, they become unsaturated and are converted into asphalt by polymerization or oxidation. This conversion is due in part to a change in the chemical composition of the hydrocarbons involved, and is observed in all cracking processes. Organic theories concerning asphaltic bitumen assume that either oxidation, polymerization, or dehydrogenation alone is sufficient to explain the phenomenon. Formation of dissociation groups from the hydrocarbon, *e.g.*, $:\text{CH}:\text{CH}_2$, is assumed. By the oxidation of the dissociated radicals, carbon may be formed.¹⁵⁷ Oxidation of paraffinic hydrocarbons gives fatty acids containing one-half the original number of carbon atoms, but non-paraffinic hydrocarbons yield water, carbon dioxide and carbon monoxide. Asphalt is prepared by oxidation of a mixture of distillation residues, freed from lubricating hydrocarbons, and a highly viscous cylinder oil of 190 sec. Saybolt at 210° F.²¹¹ Fine-grained asphalt may be obtained when melted asphalt at a temperature of 105-260°, depending upon the softening point, is mixed with a liquid hydrocarbon boiling below 0°, for example, propane. On entering the receiver, propane evaporates and fine-grained asphalt drops to the bottom.²¹⁰ Murez^{150a} states that asphalt may be prepared from mazout distillate residues, treated with dehydrating agents, at high temperature, with stirring; the unsaturated compounds formed are polymerized to asphalt-like substances by further heating without cracking. Nellensteyn¹⁵⁷ pointed out that the cracking process should not proceed to the separation of coke,⁹³ but that a limit should be set depending on the origin of the colloidal carbon in the organic protective medium. Therefore, asphalt is to be considered as a stable oleosol.

Standard Oil Co. (McConnell^{209a}) prepares asphalt of better quality from distillation residues of petroleum by treating with oxygen-containing gas at 400-550° F. Catalytically acting substances containing an acid-forming element are introduced into the mass with the gas. The catalysts used are: SeS, SOCl₂, SO₂F₂, POCl₃, POF₃, PSF₂, and SiHF₃.

Berl's experiments^{31a} have shown that cellulose and other carbohydrates may be converted under definite conditions into asphaltic bodies.

On the basis of these results, Berl developed a theory of petroleum origin according to which asphalts are not the oxidation products of petroleum hydrocarbons, but originate from cellulose and other carbohydrates. The colloidal carbon particles are lyophilic, and are protected by a surrounding medium; because of the colloidal carbon, the color of asphalt is a dark chocolate brown. Wischin²⁴⁸ attributed the dark color of the crude to an internal molecular rearrangement of the acid asphalt, and assumed that heavy hydrocarbons, such as asphalt and asphaltenes, were present in the oil in colloidal dispersion.

Sherrick¹⁹⁷ contended that the hydrated earthy material, which adsorbs the heavy asphalt of the crude oil, forms an oil-soluble colloid (similar to precipitated hydrous ferric oxide), and that the water globules are encased in tough, elastic membranes of this colloid. Richardson¹⁸¹ found such an oil-soluble colloid in Trinidad asphalt, and reproduced it by mixing a water solution of a colloidal clay with asphalts and asphalt oils, driving off most of the water by heat. Richardson further assumed that some of these processes took place during the formation of crude petroleum, leaving it charged with such an oil-soluble colloid, which later served as an emulsifier when the crude oil came into contact with water under conditions favorable to emulsion formation. It has been proved that when asphalt is removed by an organic solvent from the earthy material, it transforms that substance from an oil-soluble colloid to a colloid insoluble in oil, which loses its protective action in water-oil emulsions. These naturally occurring colloidal dispersions found in Trinidad asphalt contain about 25 per cent of finely divided mineral matter; but artificial mixtures of bitumen and dispersed clays can be made with a mineral content as high as 60 per cent.

Nellensteyn¹⁵⁶ described asphalts as protected lyophobic sols, in which micelles forming the disperse phase are composed of hydrocarbons of high molecular weight and high carbon content, presumably enveloping nuclei of free carbon. It is assumed that the disperse phase is composed of asphaltenes insoluble in naphtha (86° Bé). The continuous phase contains hydrocarbons of low molecular weight, which are soluble in naphtha (86° Bé; petrolenes).

Mack¹⁸⁴ considered asphalts as sols of asphaltenes in a mixture of asphaltic resins and oily constituents (petrolenes). Asphalts, both natural and artificial and of various origins, possess varying ability to emulsify water. In this respect, asphaltic residues from crude oils are considered inferior to natural bitumens. Asphaltic bitumen, as well as asphalts, find wide application in spraying processes, for which they must be heated to very high temperatures to reduce them to a thin liquid; the emulsifying ability of asphaltic bitumen is of great importance in practice.

Graefe and Fleck⁸² pointed out that the expression "asphalt emulsion" is incorrect, for the term "emulsion" is defined as an intimate mixture of two immiscible liquids. Asphalt, on the other hand, is a solid bituminous substance, a mixture of hydrocarbons, which exists in water as a suspen-

sion at ordinary temperatures. In Alexander's "Colloid Chemistry"* it is stated that asphalt in water forms emulsions and not suspensions.

It has been ascertained that the consistency of a dispersed system, such as a bitumen emulsion, is regulated not only by the phase-volume ratio, but by alteration of the particle size or size distribution of the disperse phase. Terry, Gabriel and Blotte²²⁰ patented the production of a "pourable" fluid bitumen emulsion having high bitumen content by producing in the system both large and small dispersed particles. The low viscosity of the emulsion they interpreted by the packing effect of the large and small particles. Traxler²²⁹ attempted to explain the mechanism by which the change in particle size distribution influences the consistency of the dispersed system. He stated that particles of various sizes in a dispersed system give a more compact mass for any given packing arrangement than do those of a uniform size. Since the volume of the continuous phase is the same in both cases and equals the volume of the interstices associated with the packed dispersed particles, the packing is looser in the system containing particles of various sizes, and this system is more fluid. In a system of lower consistency there are fewer points of contact and larger films of continuous phase between the dispersed particles. Traxler prepared two bitumen emulsions, each composed of 60 parts by volume of asphalt dispersed in 40 parts of a dilute soap solution. Emulsion A contained particles of a quite uniform size (most of which were less than 1 micron in diameter) and had the apparent viscosity of 41.5 seconds at 25° C (Saybolt-Furol viscometer). Emulsion B contained droplets of asphalt most of which were 2 or 3 microns in diameter. The viscosity of this emulsion measured 36 sec. at 25° C.

Emulsions A and B were blended in various proportions and the viscosity at 25° was determined for each mixture. The values are recorded in Table 1 and Figure 1.

Table 1. Viscosity at 25°

Volume Per cent		Sec.	Volume Per cent		Sec.
A	B		A	B	
0	100	36.0	60	40	21.5
10	90	23.0	70	30	24.5
20	80	21.5	80	20	26.0
30	70	20.0	90	10	33.0
40	60	19.5	100	0	41.5
50	50	20.5			

Although the various mixtures contain the same proportion of bitumen and soap solution, they are more fluid than the original component emulsions because of their greater non-uniformity of particle size.

Traxler and Coombs²³⁰ attempted to show that anomalous flow characteristics depend not only on the type of bitumen used, but on the temperature, method, and degree of processing to which the asphalt has been subjected. While some investigators assert that asphaltic bitumen

* Vol. III, p. 543. New York, Chemical Catalog Co., Inc. (Reinhold Publishing Corp.).

is truly viscous, others state that it exhibits non-Newtonian flow characteristics. If the flow characteristics of asphalt are complex, an exceedingly involved physical structure and chemical composition are indicated. The presence and degree of abnormal flow expressed in such characteristics as thixotropy, age-hardening, quasi-viscosity, and elasticity depend on the source of asphalt, degree of processing and temperature and rates of shear at which the measurements of flow are made. The rate of shear influences the physical structure of the system. All types of

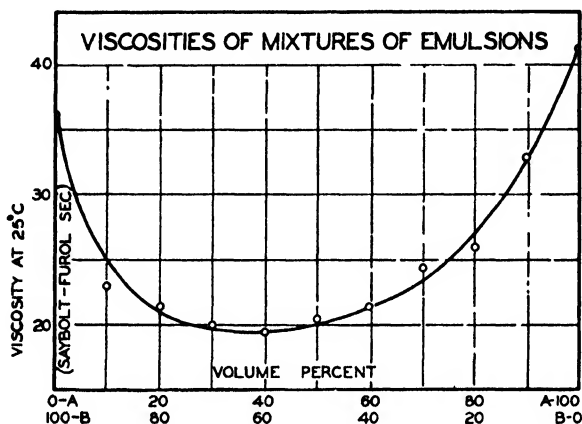


FIG. 1.

asphalt, whether viscous or not, show gradual formation of an internal secondary structure, which is unstable toward heat and mechanical influences. Age-hardening is evidently proof that asphalts are of a colloidal nature. As a phenomenon, age-hardening is thixotropic in nature, because it has been found that, by applying high shearing stress in a rotating cylinder viscometer, the viscosity of an aged asphalt could be reduced just as it is done on heating. The average shearing stress applied was 34,800 dynes per square centimeter, or 69,600 dynes per square centimeter.

Nellensteyn^{159a} discussing the critical surface tension of asphalt bitumen and tar solutions, states that the ultramicroscopic investigation of asphalt bitumens indicates that such solutions appear as two-phase systems. When organic solvents are added, the disperse phase combines. But, in this case, precipitation in the colloid-chemical sense, not solubility, is involved. According to Limburg's experiment,^{130a} the interfacial tension micelle/medium is essential to stability. This interfacial tension is not known. Antonow's rule gives help in the choice of both flocculating and peptizing reagents. If γ_{f1g} and γ_{f2g} are the surface tensions of the two phases, then the interfacial tension is $\gamma_{f1f2} = \gamma_{f1g} - \gamma_{f2g}$. A decrease in surface tension γ_{f2g} causes increase in the interfacial tension, thereby decreasing stability. A coagulating agent always

possesses a low surface tension, while an asphalt bitumen micelle, in all probability, has a high surface tension. If solvents which are miscible with the medium, as well as with the stabilizer of the asphalt bitumen, were arranged according to the value of their surface tension, the relationship between surface tension and flocculating, as well as peptizing action, would be apparent. The $\sigma-t$ curve^{150b} of asphalt bitumen and similar systems is significant in recognizing the relationship between the critical surface tension of an asphalt bitumen solution and that of the asphalt bitumen itself.

For an effective coating, asphalt should penetrate but little, its principal function being to form a water-tight skin over the surface with which it is brought into contact. Practice indicates that the larger the asphalt particles, the heavier the asphalt skin and the smaller the coverage. The smaller the particles (the finer the distribution) the larger the surface covered by an equal weight of asphalt. The asphalt skin obtained from a finely divided emulsion necessarily contains more emulsifying agent per gram of asphalt and probably contains more per square feet of skin (this depending upon the relative increase of interfacial area and of "skin" area, as particle size of the emulsified asphalt is decreased).

Emulsified asphalts consist in general of asphalt, 45-75 per cent; water, 25-55 per cent, and emulsifier, 1-10 per cent.¹⁹⁰ An accurate knowledge of the content and nature of soluble materials present in the water phase of an emulsion system is necessary, because electrolytes are intimately associated with the emulsifying process. Stable asphalt emulsions are similar to other types of emulsions in that they are prepared with soaps, clays and alkalies. There is a definite dynamic dispersion characteristic of the asphalt-water system,¹⁸⁶ as well as a definite mode of action of the emulsifying agents in stabilizing the asphalt/water interface.

Defining the degree of dispersion as the reciprocal of the average diameter λ of the particles (expressed in microns), Nasini and Rossi^{152a} determined microscopically the size and distribution of the particles of bitumen emulsions. The degrees of dispersion were found to vary from 0.25 to 0.50. In turn, the degree of dispersion has been considered as a measure of the index of workability.

Asphalt-water systems, suitable for road work, must meet certain requirements, in the form of weathering "tests." They must remain liquid without separation for an indefinite period before application. Three or six months are usually considered sufficient, although more stable systems have been used. Mechanical stability and good penetration within ordinary limits are not the only characteristics of a paving asphalt: resistance to the action of water, to destruction by freezing, and to cracking by contraction and expansion are also of importance. Asphalt emulsions must flow freely under all weather conditions. They must break down soon after application, leaving a layer of pure asphalt which thoroughly covers and bonds the mineral aggregate. Certain emulsions

which must be dried in order to break down and become effective as a binder are not suitable as paving materials. The most successful asphalt emulsions are those which, when in contact with aggregates, break down when exposed to air.

According to Ross,¹⁹⁰ most of the straight residual petroleum products are either lacking in their ability to penetrate the surface of a road bed or, if they are sufficiently fluid to penetrate, they do not set or harden as rapidly as they should. Softer grades of asphalt cements show a considerable advantage, producing a mat surface by the addition of mineral matter. "Cut-back" asphalts are recognized as the most promising types among surface-treating materials. These are prepared by fluxing asphalt with gasoline or some heavier and less volatile distillate. "Cut-back" asphalt sets rapidly after application, at times too rapidly to permit satisfactory penetration, particularly of gravel, shell, top soil or other road-bed materials. Gasoline is not as good a solvent for asphalts as are the heavier distillates, such as naphthas and kerosene. When relatively high flash-point distillates are used for cutting back asphalts, rapid hardening of the material must be prevented if good penetration is to be secured. The mineral aggregate of a road bed adsorbs the heavy asphaltic constituents, causing a separation which permits a portion of the distillate to penetrate further into the structure. Cracked residues, produced by the modern cracking process, yield asphalt from oils containing practically none originally.

In general, it has been assumed that the production of paving asphalts from paraffin-containing crude oils is impossible, or at least very difficult. If asphalt is separated by refining rather than by distillation, a slightly smaller amount of paraffin is found in it. Asphalt-containing mineral oil is subjected to distillation, first at ordinary pressure and then in a high vacuum (1 mm remaining pressure), and paraffin is determined in the distillate according to Heinze and Zwergel.²⁵²

Adhesion of asphalt emulsions to sand and mineral aggregates has been discussed by J. Jacksel.¹⁰⁶

Concerning the elasticity of asphalt, Marcusson¹³⁸ pointed out that crude asphalts are similar to natural asphalt deposits. He also stated that crude oils with a high paraffin content, such as Pennsylvanian and Galician, have the least binding ability and the least elasticity. Richardson¹⁷⁹ is in accord with Marcusson. However, Abraham¹ and Hausmann⁹³ are of the contrary opinion, for they point out that no relation exists between the paraffin content and the quality of the asphalt, and that the paraffin content is of importance only insofar as it indicates the origin of the asphalt. Paraffin has never been found in asphaltene, seldom in natural asphalt, only in traces in artificial asphalt from asphalt-containing petroleum oils, but more or less in asphalts obtained from crudes of semi-asphaltic or non-asphaltic composition.

Zaharia and Sucabu,²⁵⁰ experimenting with five Roumanian crude oils, assumed that paraffins and resins are not in a colloidal state in the crude, but that asphalt is. To prove the correctness of their assumption,

quantitative ultrafiltration was carried out with a Büchner apparatus at 150 atmospheres, using Vulkan vulcanized rubber membranes 0.04 mm thick, which were laid on top of two or three sheets of filter paper, and the whole placed over a perforated plate. Hard and soft asphalts were retained completely. The filtrate did not give a precipitate with benzene and ethyl ether, but the asphalt was soluble in benzene, in which it was freed from resins and ultra-filtered. The asphalt obtained and dried was soluble in the ultra-filtered oil.

The Metan Spolka¹⁴³ patented a method for separating asphaltic substances from crude oil by mixing it under pressure with liquefied hydrocarbons from natural gas having a critical temperature below 5°-8°. The amount of the crude oil mixed was five times that of the liquefied hydrocarbons, and about 13 per cent of paraffin-free asphalt was separated. In the refining process, the crude naturally occurring asphalt is usually subjected to a temperature of 325° F, which removes the water and results in a refined asphalt containing 57 per cent of bitumen, 39 per cent of mineral matter, and 4 per cent of water of hydration of mineral matter. The mineral matter passes through the finest filter, and under an ultramicroscope is found to consist of clay in a colloidal state, which had its origin in the mineral matter of the mud spring and was introduced into the bituminous phase on the removal of the water by refining. The amount of mineral matter in the colloidal state depends on the concentration of the continuous phase. In refined asphalt, actually all the mineral matter at ordinary temperature may be regarded as colloidal, separating out under suitable conditions.¹⁸⁰ Richardson lists the following composition for the natural asphalt found in Pitch Lake, Trinidad, British West Indies:

Substance	Per cent
Bitumen	39
Mineral matter	27
Water and gas, volatile at 100 (°C)	29
Water of hydration of mineral matter	5

The water which separates from asphalt on melting contains large proportions of sodium chloride and sulfates of sodium, ammonium and iron, as well as borates and iodides, and small percentages of potassium, calcium and magnesium salts.

Richardson¹⁸¹ describes an improved process for the dehydration of crude lake asphalt which contains a high percentage of water. This process dehydrates, without the aid of heat, by thoroughly grinding or pulverizing the crude asphalt, after which it is either exposed to the atmosphere or subjected to an artificial drying process, using acid in vacuum. About 30 per cent of water is driven off in 24 hours.

In the University of Delft,⁴⁷ asphalt emulsions of the oil-in-water type were studied. De Kadt¹⁰⁸ investigated the water-in-oil type of emulsion found in Mexico, namely Zacamixtle and Panuco crudes, and found that their water content ranged from a low percentage to as high

as fifty per cent. He attempted to convert water-in-oil into oil-in-water asphalt emulsions by the use of potassium oleate, basing his assumption on the theory of inversion promoted by Clowes. The method failed, however, the coagulated asphalt being too soft because of the presence of gasoline. Inversion by distillation was proposed by Waterman,²⁴¹ but frothing accompanied this process. Rosin soaps were substituted for alkali oleates, rosin oil having a distillation range of 280-340° being used. Rosin oil was dissolved in the crude-oil emulsion by stirring and the mass heated up to 40-60°, with addition of potassium hydroxide. A 1.15 per cent rosin oil was used, but 0.7 per cent is equally effective, the quantity depending on the degree of dispersion and the percentage of water. Distillation is carried out with superheated steam or a mixture of hot gases, such as air and nitrogen. de Kadt states that the addition of 0.5-1.0 per cent of an ordinary soap (oleic acid-sodium hydroxide) to the residue at 60-90°, dilution with a large quantity of water and continuous stirring results in the formation of an asphalt emulsion. Thus distillation and action of soap when combined lead to inversion of phases.

Illing and Kelly¹⁰⁰ distilled petroleum to obtain asphalt by pumping it through heated tubes, conducting it to an electrically heated or superheated steam evaporator where it was passed over a series of plates; the vapors were drawn off and condensed. The residue was heated with a stream of hot air and converted into asphalt; its vapors were also condensed. If heating exceeded 600° F, cracking of the oil took place.

Streppel²¹⁵ patented a method for extracting asphalt from oil sands having a high asphalt content, by heating with oil above 100°. The Sun Oil Company²¹⁷ prepared highly viscous asphalts from non-viscous petroleum residues by heating under vacuum to temperatures higher than the critical temperatures of the lightest oils, and at the same time leading low-boiling vaporized hydrocarbons through the oil, which flows slowly in a wide, thin layer over a surface heated by mercury vapors. Thus the light oils are distilled off, leaving a highly viscous product, which is discharged.

The black or dark-colored bituminous matter in asphaltic-base oils may be readily coagulated by means of strong sulfuric acid.^{114a} The chemistry of sulfuric acid treatment has been investigated by Brooks and Humphrey,³⁷ who found the accepted view, that olefins are polymerized to tar and removed as sludge, to be erroneous. Pure olefins up to sixteen carbon atoms do not give tars with sulfuric acid of 100 per cent concentration. Dunstan⁵² considers the formation of acid tar as a "dual" phenomenon, *i.e.*, the acid coagulates the colloidal matter present in the oil, polymerizes olefins and diolefins, sulfonates aromatic derivatives, and oxidizes the original substance.

The emulsified state of both natural and artificial asphalts is due to the presence of emulsifiers, in the former to clay and other substances, in the latter, to naphthenic acids, rosin, sulfonated oils, casein solutions, and alkalies and acids in general. Two types of emulsifier are used in the production of commercial asphalt emulsions; (1) alkali:alkalies, alkali

silicates, alkali soaps of fatty acids and oxy-acids obtained from solid paraffins by oxidation with air or oxygen; and (2) acid: sulfonated fatty acids, oxy-acids and inorganic salts, such as aluminum chloride. If asphaltic bitumens contain a sufficient percentage of naphthenic acids, alkali hydroxides are used for emulsification. Alkali emulsifiers are often used in combination with proteins. It is assumed that some of the hydrolysis products of soaps used as emulsifiers form a protective film, and this is true of proteins in particular.

Most of the commercial asphalt emulsions are of the oil-in-water type in which the asphaltic bitumen or tar is dispersed in the water phase, containing soaps of fatty acids, resins, etc. However, the type of emulsion depends, of course, on the nature of the emulsifier, that is, alkaline earths form oil-in-water emulsions, and calcium and magnesium salts of fatty acids form water-in-oil emulsions.

Since the consumption of asphalt emulsions exceeds the production of natural asphalts, artificial asphalts have been prepared from "asphalt-bases," as well as by distillation and oxidation of mineral oils. The fact that artificial asphalts have been accepted in general practice necessitates the perfection of a process whereby asphalt can be made into a stable emulsion.

Emulsification of Asphalt and Bitumen

Flavigny,⁶⁶ in his investigation on the formation and stabilization of bitumen emulsions, pointed out that both depend (a) on the nature and amount of active substances present in the bitumen and (b) on the ability of these substances to form a film which covers the surface of the dispersed bitumen globules. In general, bitumens contain a rather large proportion of active substances. Bitumens that contain sufficient active substances give stable emulsions with soda or caustic potash; otherwise a stabilizer is required. If the bitumen has sufficient active substance to lower the interfacial tension between the bitumen and the aqueous phase, then a fatty acid may be added to the bitumen and soda or potash to the aqueous phase to form a film sufficient to stabilize. If the interfacial tension between the bitumen and the aqueous phase is too high, an emulsifying agent perfectly soluble in the bitumen must be added to it, and the asphaltenes and paraffins must be dissolved at the same time in such a manner that a homogeneous distribution is obtained.

Flavigny proved by his experiments that the acid value of a bitumen is not solely indicative of the emulsifying power of the active agent present in it, but that its molecular weight must be considered as well. Acids of low molecular weight always possess an emulsifying ability, while acids of high molecular weight have instead a stabilizing power.

Lange¹¹⁹ distinguished between emulsifying and stabilizing agents by classifying emulsions into two groups, namely: (1) those in which emulsification is caused by a chemical action, *e.g.*, the formation of soaps, and simultaneously decreases the surface tension, bringing about also a change in the electric charge of the particles; and (2) those in which

stability is secured by an inert agent not manifesting any chemical action in the interface. These emulsions are similar to the preceding groups of emulsions with regard to solubility in the aqueous phase, but are distinguished by their inability to exchange ions, which is characteristic of emulsions resulting from chemical action. The stability of these emulsions is the result of adsorption of solid, insoluble particles in the interface. True stabilizers have a feeble emulsifying ability, and such is the case with gelatin or casein. Likewise, true emulsifiers may possess a protective, stabilizing power, for example, alkali soaps and sulfonates. According to Flavigny, this classification may assist in the choice of substances to be added and utilized in the preparation of bitumen emulsions.

An inactive bitumen cannot be permanently dispersed in an aqueous phase that does not contain a stabilizer and an emulsifier. In the case of active bitumens, a stabilizing agent is used and an inert emulsion is formed. The importance of particle size and of the laws of colloidal chemistry in evaluating the adhering strength and quality of bitumen emulsions has been emphasized by Kresse.¹¹⁵

In the preparation of asphalt emulsions, the melted bitumen, or tar, is usually mixed with a hot, aqueous solution of the emulsifier. If fatty acids and alkali hydroxides are added, a protective soap film is always formed during emulsification. Grinding facilitates dispersion of asphalt. To increase the dispersion of an emulsion, colloid mills of various types are employed. The Hurrell mill (described by Clayton⁴²) is well adapted to the mixing of the individual components comprising an asphalt emulsion. While it is possible to use emulsified asphalt for road construction for about nine months of the year, non-emulsified asphalt can be used only in dry weather and for four to five months. Two processes¹²⁰ are used to prepare emulsified asphalts: (1) by forcing the emulsified liquid, namely the hot bitumen in water, through a colloid mill at 2000-4000 r.p.m.; and (2) effecting the emulsification by direct action on the bituminous mass using various soaps as emulsifiers. Variations in the components, particularly emulsifiers, as well as in the mode of emulsification and physical conditions under which emulsification takes place, characterize differences in patents. Mann¹³⁷ patented a process for the emulsification of asphalt in a soap and starch mixture heated with water until decrepitation of the latter. The hot bitumen is dissolved in benzene, or any other suitable volatile solvent is poured over it. A nozzle arrangement at the bottom of the container provides good mixing. The dissolved substance remaining is dispersed in the mixture; the volatile solvent evaporating on entering the hot mixture is recovered by condensation, and the mixture is allowed to cool with continuous stirring to obtain a homogeneous emulsion. Albert and Berend⁶ devised a method for using a thick, neutral or slightly alkaline cellulose as an emulsifier. They added 5 parts of the latter to 9.5 parts of fluid tar to effect dispersion. Another patent issued to these investigators⁷ presents a method for solidifying emulsions of asphalt and tar oils when these emulsions

contain only a small amount of colloidal material and a substance producing hydration. This process is irreversible. Mullin¹⁵⁰ emulsifies asphalt by allowing an emulsifier, such as a soap solution, to flow into a receiver containing the amount of asphalt to be emulsified and not exceeding that of the emulsifying agent by four times, and heats it gradually. If larger amounts are to be treated, the process is repeated.

Plauson's Forschungs Institut¹⁷⁵ emulsified asphalt or pitch by heating it to the melting point and working up the fused mass with water in a colloid mill until a colloidal dispersion was formed. Humic acid or its compounds, in an amount of from 1 to 2 per cent, when added to the water pitch or asphalt during the dispersion process, assist the stabilization to a considerable extent, and lead to the formation of stable emulsions with a 35 to 40 per cent concentration of the disperse phase. The Bataafsche Petroleum Maatschappij²⁰ prepared asphalt emulsions by mixing asphalt, preferably in a molten state, with hydrocarbon oxidation products and emulsifying the mixture with alkali or alkali salt solutions at a temperature of 90 to 100° C. The hydrocarbon oxidation products used as emulsifiers contain, beside the unchanged hydrocarbon, acids, anhydrides, lactones, alcohols and esters. Another process for asphalt tar and pitch emulsification is given by Low,¹³³ who prepared a mixture of tar oil and emulsifiers and separately a mixture of casein, resin, sodium hydroxide and water, which was treated until completely saponified. The first mixture was then poured into the second mixture with slow stirring.

The Asphalt Cold Mix, Ltd.¹¹ prepared aqueous bitumen emulsions by mixing the bitumen with an emulsifying agent obtained by the action of alkali upon proteins and stirring the mixture. The Bataafsche Petroleum Maatschappij²¹ emulsify asphalt by the use of hydroxides, alkali carbonates and ammonia. Summerfield²¹⁶ makes asphalt emulsions by pouring melted asphalt into a boiling alkaline water solution and adding about 1 per cent of oleic acid or other unsaturated fatty acids, such as linoleic from linseed oil, completing the emulsification by adding asphalt until the desired concentration is obtained. Thornley and Delaware Co.²²⁷ have a similar process for the emulsification of pitch and other unsaponifiable substances. Basset and Szidon¹⁰ prepare asphalt emulsions by mixing whale oil with water containing potassium hydroxide and a small amount of mucilage. The mixing is carried out in a colloid mill. The Asphalt Cold Mix, Ltd.¹² claim that a very good emulsion results by mixing asphalt at 100 to 110° F with 2 per cent of oleic acid or other unsaturated fatty acid, then with a quantity of about 5-per cent aqueous solution of alkali silicate or borate approximately equivalent to the quantity of bitumen, and stirring vigorously. Asphalt with a weight of 25 per cent of a 15 per cent sodium silicate solution may be emulsified in 1000 g of water and 100 cc of a 1-per cent aluminum chloride solution. The aluminum chloride can be replaced by aluminum hydroxide. Another patent¹³ recommends treating asphalt containing 30 per cent of aromatic compounds with 5-per cent sulfuric acid and, after separating the asphalt, sulfonating with 10 per cent of 20-per cent oleum. The acid

sludge is removed and neutralized with sodium hydroxide or sodium chloride. The free sulfuric acid is salted out with barium chloride from the sulfonated mixture. Nine parts of the mixture obtained are dissolved in 300 parts of water and emulsified with 800 parts of asphalt under pressure and heat. The resulting emulsion is stable in hydrochloric acid solution or in the presence of salt solutions or lime. Asphalt emulsions have been obtained⁵³ in the following manner: Venezuela crude petroleum was distilled and neutralized with sodium hydroxide, the residue treated at a high temperature with hydrochloric or sulfuric acid in an amount equivalent to the alkali used, redistilled, and mixed with 100 parts of Venezuela asphalt. The melted mixture was emulsified with 80 parts of a 0.5-per cent sodium hydroxide solution, with stirring.

At a temperature not higher than 100°, Halvorsen and Travis⁹⁰ emulsified asphalt by melting it with a small amount of a mineral substance and then stirring the mixture into hot water containing 0.75 per cent of an alkali phosphate, preferably sodium phosphate, in which it was finely dispersed. Kirschbraun¹¹⁰ prepared stable bitumen emulsions from melted asphalt by mixing it with and stirring it into water containing clay. These emulsions were stabilized either by sodium sulfite or zinc sulfate. Headley⁹⁴ heated fatty acids and oils, such as linseed or other drying oils, for about 2 hours and saponified the mixture with sodium carbonate in an amount 20 to 50 per cent by weight of the oil (after cooling to a lower temperature). The alkali may be added before heating to a high temperature. The soap obtained was stirred with asphalt and water. The material obtained was particularly stable to temperature changes.

Elosegui⁵⁶ prepared asphalt emulsions by adding a bitumen containing 1 to 3 per cent of organic acids. The concentration of the asphalt in the emulsions was 25 to 50 per cent. Crown Rock Co.⁴⁵ pointed out that tar or pitch resulting from oxidation or drying of petroleum called maltha—a black, viscid substance intermediate between petroleum and asphalt, having a strong bituminous odor—is a suitable emulsifier. It is mixed with water containing finely divided silicon oxide and stirred vigorously with asphalt. Montgomery¹⁴⁶ melted Mexican asphalt, which is a solid at ordinary temperature, and poured it into a dilute sodium hydroxide solution, with stirring. Ebberts⁵⁴ states that silica, iron oxide and gypsum promote the formation of asphalt-in-water emulsions, and that limestone, magnesium carbonate, calcium hydroxide, magnesium hydroxide and portland cement promote the formation of water-in-asphalt emulsions. Kirschbraun¹¹¹ dispersed melted asphalt in a suspension of clay, such as bentonite, in water, continuously agitating the product in a mechanical mixer. Morrell¹⁴⁹ produced stable asphalt emulsions by adding to an emulsion of an oleaginous material a suspension of a non-fluid, pitchy, asphaltic or bituminous material. The coalescence of the non-fluid particles of the suspension with the oily globules of the emulsion gives a stable emulsion. Emulsions of tar, asphalt, pitch, etc., insoluble in water, are prepared by using soap insoluble in water as an emulsi-

fying agent.¹⁸ Tribasic sodium phosphate, not exceeding 0.75 per cent, is used in effecting emulsification of asphalt and water.⁸⁹ Asphalts, tars, and petroleum residues may be emulsified with the sodium, potassium, or ammonium salts of fatty acids or resins, to which are added organic substances, such as low molecular weight alcohols or ketones of the fatty acid series, B_2OH or $PhOH$, capable of lowering interfacial tension between the bitumen and water.⁸⁸ It may be particularly advantageous to use mixed dispersions which contain such dispersing agents as are not affected or redissolved by water once the dispersion has been allowed to dry. Into 200 parts of a 30-per cent paste of finely ground cellulosic material, such as lignite, containing humic acid is caused to run, at a temperature of between 40 and 50°, the fused mass of 500 parts of petroleum asphalt having a temperature of 80° and a softening point according to Krämer-Sarnow of 50-60°, while vigorously stirring and adding 300 parts of cold water in such a manner that the temperature of the dispersion produced does not exceed 50°. ⁶³ Bitumen emulsion may be prepared when soft bitumen, containing a small proportion of a saponifiable material, such as oleic acid, is melted and thoroughly mixed with a suspension of powdered hard bitumen suspended in water containing a small proportion of sodium hydroxide. Depending upon the desired hardness of the product, the proportion of hard bitumen used (7-20 per cent of the soft bitumen) is varied.¹⁴⁰

An emulsifying agent for tar, bitumen and the like is prepared by heating a mixture of amylaceous and saponifiable substances with an alkali substance. For example, four parts of residual vegetable oil from paper manufacture, 1 part of maize starch and 25 parts of water are heated to 50° with stirring. A 7-per cent solution of NaOH (17 parts) is added and the mixture heated almost to boiling.²⁰⁵ An emulsifier consisting of equal parts of pulverized, water-free cereal and/or linseed oil or soybean oil dispersed in benzene serves to prepare an asphalt emulsion. Three parts of this emulsifier are mixed in a stirrer with 97 parts of melted asphalt. At the place of use, the mixture is combined with 15 per cent of water in a heated emulsifying machine. If larger amounts of water are to be incorporated, the amount of emulsifier must be increased accordingly.⁹⁶

Besides soaps, alginates and the like, or turpentine resins formed by the distillation of turpentine, may be used as emulsifiers for bitumen emulsions. Resin tars saponified by an alkali solution are recommended for the same purpose.¹⁹⁴

Proteins, pectins, polysaccharides, hemicelluloses, gums, tannins, and clays are considered as emulsifying agents for bitumens. According to Rick,¹⁸³ the emulsifier remains dispersed in the bitumen, after evaporation of water, as a filiform structure which can modify the elastic, thermal and aging properties of the bitumen. Lechler¹²² reported that emulsification of asphalt is effected if a solution of an alkali, such as the carbonate or the hydroxide of sodium or potassium, and a saponifiable substance, such as a fatty acid, is added to a molten mixture of asphalt in

successive amounts of varying concentration. Most of the alkali is added at an early stage of the process. In another patent Lechler¹²³ recommended heating bitumens, adding wool fat or resin as emulsifier, and mixing it at the same time with an aqueous alkali solution.

Fox⁷¹ effected emulsification of liquefied asphalt in the following ways. (1) By using soaps, together with higher monohydric aliphatic alcohols. The soaps and alcohols may be mixed as such, or may be obtained by a reaction of caustic alkali with a liquid animal wax, such as sperm oil; protective colloids or stabilizers may also be added to the emulsions. (2) By using similar bituminous materials, emulsification is produced by emulsifiers obtained by treating liquid marine animal waxes or fats, containing esters of monohydric aliphatic alcohols, with sulfuric or phosphoric acid. Vereinigte Dachpappen A.-G. and U. Bräutigam²³⁷ patented the preparation of an aqueous bitumen emulsion. One-thousand parts of bitumen, particularly asphalt, are heated to 90° with the addition of 60 parts of Swedish resin and 100 parts of hot water with continuous stirring at 80-90°. After the resin soap has been completely formed, 800 parts of water are added.

Malchow A.-G.¹³⁵ claims that emulsification of bitumen and water occurs when potassium soaps or isomers of abietinic acid, such as pineabietinic acid, are used. These resin acids are obtained from tallow oil by treatment with petroleum ether. The amounts mixed in the homogenizer are: 100 parts of bitumen, 4 parts of potassium hydroxide and 6 parts of isomers of abietinic acid. The resulting bitumen emulsions retain their stability in transportation as well as in storage.

Zsigmondy²⁵¹ proposed low-melting, readily emulsifiable bitumens of low viscosity as emulsifiers for high-melting bitumens, such as tar asphalt and petroleum pitch. By weight, 1 part of saponin, 5 parts of bone glue, 10 parts of 70-per cent silicon oxide, 4 parts of water glass and 8 parts of low-melting bitumen are mixed together and stirred. One part of the low-melting bitumen is melted with 9 parts of water and 12 parts of high-melting bitumen.

As emulsifier in preparing bitumen emulsions Societa Anonima Permolio²⁰³ uses an acid sludge obtained by refining mineral oil, especially white oil, with sulfuric acid. The purification is carried out by means of water vapor at 120-130°, by heating with water, or finally by using water and sulfuric acid, followed by settling.

N. V. de Bataafsche Petroleum Maatschappij²² uses as emulsifiers solid colloids, such as clay or bentonite, and aqueous emulsions of asphalt acids and salts. Protective colloids such as gum and glue are added.

Wintsch²⁴⁷ in his patent specified latex as an emulsifier in making bitumen or asphalt emulsions.

Colas Products, Ltd.⁴³ dispersed bitumens in a colloid mill using potassium oleate as emulsifier. The finished emulsion contains about 85 per cent of bitumen with particles 20-30 μ .

I. G. Farbenindustrie A.-G.^{60a} effected emulsification with humic acids

as emulsifiers. When brought on the surface these emulsions proved to be of high stability. Plant-production equipment was used.

Novak,¹⁰¹ in emulsifying tar, asphalt, or chlorine derivatives of oils, used in addition to an emulsifier a protective colloid such as glue, casein, resin and naphthenic acids.

Soc. Chim. de la Route²⁰⁴ claim the production of stable asphalt emulsions from petroleum distillate residues by mixing with heavy petroleum in such an amount that a liquid mixture is formed at 15°; this is stirred with an alkaline solution, for example, a water-glass solution.

Lewis¹²⁸ applied as emulsifier a gel of aluminum hydroxide admixed with finely divided sand, dolomite, iron oxide, chromium yellow, chromium green and Berlin blue, the emulsifier being stirred continuously with water and melted bitumen added. This type of emulsion prevents corrosion of the walls of containers by acids.

Neushabel Asphalt Co., Ltd.¹⁶⁰ prepared bitumen emulsions from Trinidad Lake asphalt by diluting petroleum residues or similar liquefying agents with tar oil and adding sodium hydroxide, potassium hydroxide and resin, for example, colophonium.

Bitutect Inc.³⁴ emulsifies asphalt by mixing at 50° F in a saturated solution of carbon tetrachloride with an aqueous suspension of colloidal clay acidified with a weak organic acid. The solution of bitumen is precipitated by acetone with continuous stirring.

Bataafsche Petroleum Maatschappij²⁴ disperse asphalt in water by heating, using an aqueous paste of bentonite (about 10 per cent) or clay and stirring rapidly.

Bendixen and Morgan²⁹ emulsified tars by using saccharides and adding xylene, carbon tetrachloride, acetylene tetrachloride and other solvents. This emulsion is suitable as a binding material for dust laying.

I. G. Farbenindustrie A.-G.^{60b} prepared emulsified tar by heating 300 parts of tar oil or a mixture of 240 parts of tar and 60 parts of asphalt from a petroleum distillate to about 150°. After 30 minutes, 40 to 50 parts of lignite grit-emulsifier (2 per cent water content) and water were added.

Gador⁷⁴ proposes a method for preparing aqueous bitumen emulsions whereby the melted bitumen is first treated with oxygen acids of sulfur, its anhydrides, acid salts, substituents, or other wastes containing sulfonic acid, such as acid tar, acid mineral tar, etc., and then mixed with water. Potassium hydroxide or alkaline salts, such as silicates, carbonates, or borates, are introduced to effect a neutral reaction.

Bataafsche Petroleum Maatschappij²³ proposed the use of colloids, such as glue, gelatin, albumin, saponin, and also sulfo-acids and starch, as successful emulsifiers for bitumens.

Rütgerswerke A.-G.¹⁹³ recommend mixing tar with highly alkaline water, containing salts of fats, resins, sulfo- or amino- carboxy-acids. The asphalt so emulsified is stable, but breaks readily when spread on a road surface.

Agthe's² invention relates to natural or artificial asphalts (Krämer

and Sarnow) mixed either with brown coal (b.p. 150-400°) or mineral oil to which is added a small amount of rubber, which facilitates emulsification. The emulsion obtained is coarse and stable.

Ebberts⁵⁵ states that substances with a high percentage of calcium phosphate assist in the emulsification of bitumens.

Thompson's²²⁵ patent for the preparation of emulsions relates to the emulsification of asphalt, provided the emulsion has a high degree of penetration and is able to solidify rapidly on exposure to air. Strict observance of the order of mixing the ingredients of the emulsion is necessary to avoid conversion of the final product into a semi-solid, spongy mass. Forty to sixty per cent of the mass is heated to 190° F with stirring, and 0.25 per cent of caustic potash, sodium carbonate or potassium carbonate is added to produce a certain degree of alkalinity. The fatty acid to be added is saponified. Asphalt to be emulsified is melted in another container, heated to 200° F and run slowly into the first mixture; 0.08-0.25 per cent by weight of oleic acid, linseed oil or whale oil used as an emulsifier is poured in. The inflow of the asphalt stream occurs simultaneously with that of oleic acid introduced into the stirred mixture.

Hunziker⁹⁷ stated that bitumen emulsions may be obtained by heating a bitumen in the presence of a solvent, such as pitch oil or petroleum, to 100° and adding at least one saponifiable fat (bone fat) and colloidal aluminum. Alkalies and also protective colloids, such as proteins or plant mucilage, may be added.

Rouault¹⁹¹ suggested producing emulsions of bitumen, pitch, or tar of the oil-in-water type by mixing tar and bitumen with 30 per cent of water, using as emulsifiers small amounts of an alkaline material capable of reacting with phenolic constituents and flour, starch or casein, rendered soluble by treatment with alkali.

The International Bitumen Emulsions Corporation¹⁰¹ makes aqueous bitumen emulsions, using a small percentage of casein as an emulsifying agent.

Dehn⁴⁶ states that a bitumen emulsion which can be mixed with aggregates and which will not break too rapidly can be produced by adding sodium phosphate to a quick-breaking, soap-free emulsion already formed, and prepared by the addition of aqueous calcium chloride or alkaline-earth metals.

Elosegui⁵⁷ melts tar with addition of wax (up to 3 per cent) and wool fat (2 per cent). To the mixture obtained, hot caustic alkali is added by stirring. This mixture may be diluted with 5 to 10 per cent of water. The addition of more water is necessary in the penetration of asphalt macadam.

Labourse¹¹⁷ prepared bitumen emulsions using as emulsifier a more or less hydrated calcium hydroxide alone or in combination with lead carbonate. The latter, which in itself is not an emulsifier, increases the emulsifying action of calcium hydroxide and otherwise influences the properties of the emulsion obtained.

Kretzer¹¹⁶ and The International Bitumen Emulsions Corporation¹⁰²

state that bitumens are usually emulsified with aqueous alkalis, stabilized with casein and the alkalinity of the emulsion reduced to about pH 8.5 by the addition of orthophosphoric acid.

Bergel⁸¹ prepared asphalt emulsions, using aqueous alkalis. Varying amounts, about 5 to 10 per cent of natural asphalt, such as Trinidad or Bermuda, rich in asphaltic acids, were used. If the asphalt content is increased above the amount necessary to obtain an emulsion, then breaking down when in contact with solid porous bodies is slower.

Standard Oil Co.²⁰⁸ prepared asphalt emulsions resistant to hard water by heating either soybean flour or gluten flour with aqueous sodium hydroxide, green acid soap and resin soap. The solution obtained is added to melted asphalt contained in a chamber equipped with a stirring apparatus. On stirring, an emulsion is formed.

For emulsification of asphalts, Bratke³⁶ used about 0.01-per cent potassium hydroxide containing about ten per cent by weight of an aromatic acid, an OH-acid, or a phenol, *e.g.*, $\text{B}_2\text{OH}_6\text{-OH.C}_6\text{H}_4\text{CO}_2\text{H}$; $\text{o-C}_6\text{H}_4(\text{OH})_2$, which is added to the asphalt before or during admixture with water. An emulsion of the water-in-oil type is obtained.

An emulsion of asphalt is obtained by precipitating asphalt with a light hydrocarbon, gaseous at ordinary temperature and pressure, for example, ethane, propane, or butane, from a crude petroleum oil containing asphalt. The light hydrocarbon may be used together with a selective solvent, such as PhOH, cresol, PhNH_2 , or furfural.²¹⁰

Grover⁸³ manufactured bitumen emulsions by using insoluble humic acid and its salt as an emulsifying agent. The stability of these emulsions is improved by the addition of 0.1 to 0.5 per cent of neutral salts, such as sodium chloride, sodium sulfate, or calcium chloride.

Gesellschaft f. Teerverwertung m.b.H.⁷⁹ proposed for emulsification of every kind of bituminous substance (tar, artificial and natural asphalts, as well as their distillation products and residues) crude products (emulsifiers) obtained by heating humus material, such as brown coal or peat, together with an aqueous alkali solution. Solid or liquid resins, fats, oils, acids, or alcohols obtained therefrom, or naphthenic acids, may improve the emulsion when added during or after its preparation. Starch, dextrin, or gums may contribute to their stability.

Gesellschaft f. Teerstrassenbau m.b.H.⁷⁸ mixes tar with about 5 to 20 per cent of resin, such as colophony or coumarone, and emulsifies the mixture in hot water containing a small amount of soap.

Sparks²⁰⁶ states that a concentrated emulsion, which can be diluted with hard water without causing separation, is made up of 2 parts of asphalt emulsified with 1 part of water, with an emulsifier containing green acid soap and either sodium silicate or tribasic sodium phosphate.

Myers¹⁵¹ proposes a mixture of molten asphalt mixed with a small amount of rosin and contacted under pressure with a stream of sodium hydroxide. The mixture, on release of pressure, is beaten and homogenized.

Hutzenlaub⁹⁹ prepared stable, highly viscous, hydrophilic asphalt emulsions by mixing asphalt with a small amount of a concentrated alkali-metal hydroxide or carbonate solution, to neutralize the free acid contained in the asphalt, and with water containing clay, stirring the mixture to effect emulsification.

Neitzke¹⁵⁵ forms an aqueous dispersion of asphalt by mixing intimately with it a relatively small amount of cottonseed oil pitch and dispersing the mixture, while heating, in a dilute, aqueous alkali solution; sodium hydroxide or other saponifying agents (alkalies) may be used. Emulsions containing 2.5 to 10.0 per cent by weight of stearin pitch, based on the amount of mineral asphalt used, have satisfactory bonding and weathering qualities.

Lichtenstern¹³⁰ heats asphalt with crude montan wax (up to 3 per cent) and crude wool fat (up to 2 per cent), running the mixture while at a temperature of 80 to 90° into a 1-per cent aqueous alkali solution warmed to 60°.

Smith¹⁰⁹ produces asphalt emulsions by dispersing asphalt in an aqueous solution of tribasic sodium phosphate; either a protective colloid or a borate may be present.

Jerie¹⁰⁷ claims that tar and asphalt emulsions may be produced by using simple alkaline resin soaps as emulsifiers.

Lechler¹²⁵ emulsified molten asphalt by stirring in 1 to 5 per cent of a concentrated solution of alkali hydroxide or carbonate and adding an aqueous clay slurry.

Hanseatische Mühlenwerke A.-G.⁹¹ recommend the use of solid alkalies instead of aqueous alkali solutions as emulsifiers.

Patent and Licensing Corporation¹⁰⁹ patented the use of ammonium naphthenates and ammonium oleate as emulsifiers in the preparation of bitumen emulsions.

Hepburn⁹⁵ dispersed 20 parts of a crude asphaltic-base oil in 9 parts of soap solution and added 78 parts of warm water containing 1 to 2 parts of a metallic salt of a fatty acid (aluminum oleate). The mixture was warmed, and 296 parts of asphalt were added slowly with stirring to obtain a uniform distribution throughout the mass.

Tabary²¹⁸ prepared bitumen emulsions by mixing 5000 liters of water at 80° with 60 to 100 kg of oleic acid and adding 35 to 70 kg of potassium hydroxide or potassium carbonate to the mixture; 1 to 2 per cent of a stabilizer, such as potassium fluoride, potassium fluosilicate, or potassium chromate, is added after saponification of the oleic acid is completed. The whole mass is then mixed with 5000 kg of bitumen at 110-140°, and homogenization of the emulsion is effected in a colloid mill.

In preparing emulsions, Ernotte⁵⁹ uses precipitated lime from sugar manufacture, containing about 80 to 85 per cent of calcium carbonate, as a dispersion medium for bitumen and tar. For dispersion of solid bitumen, this material is heated with the addition of about 50 per cent of water containing lime, and the charge is dispersed in a homogenizer.

Roederer¹⁸⁸ produced bitumen emulsions using brown coal or oil shale as the emulsifier, the latter being enriched with regard to its bitumen content before use, and treated with acids or alkalis.

Liberthson¹²⁹ manufactured bitumen emulsions, using 5 to 300 parts of molten bituminous material in 0.25 to 10 parts of aqueous sodium sulfonic derivative in 100 parts of water at 100° F. The stability of the emulsions obtained may be increased by adding 0.25 to 10 parts of colloidal clay to the emulsifier before emulsification. (The sodium sulfonic derivative is obtained by using sulfuric acid sludge from the purification of petroleum oils neutralizing with alkali, and mixing with 40 to 60 per cent by volume of aqueous ethyl alcohol and separating the sediment.)

Patent and Licensing Corporation¹⁷⁰ uses as emulsifiers residues obtained by treating colophony with petroleum ether and furfural. The resin is saponified with 0.1 to 0.5 per cent of excess alkali. A solution containing 3 to 8 per cent of rosin soap is mixed with the asphalt in a colloid mill.

The Standard Oil Co.²⁰⁹ dispersed asphalt in a dilute soap solution, such as triethanolamineoleate, about 1 per cent being sufficient if approximately 1 per cent of sodium sulfite, sodium chromate, or potassium chromate is added. Other suitable salts are sodium oxalate, tribasic sodium phosphate, sodium monosulfide and sodium thiosulfate.

McConnaughay¹³⁹ melted bitumen separately, mixed it with saponifiable material, such as "red oil" (oleic acid) and emulsified the resulting mixture by using hard water treated with an alkali metal fluoride to precipitate the calcium salts and to render the water alkaline.

Baume, Chambige and Boutier²⁸ list as emulsifiers (1) soaps formed *in situ*, (2) mixtures of different bituminous materials, and (3) inert materials like kieselguhr; sawdust may also be used.

Smith²⁰¹ recommends a 0.1 to 1.8 per cent aqueous alkali metasilicate solution as emulsifying agent for bitumen emulsions, such as pitch, tar, or similar substances, suitable for road work. Halvorsen⁸⁸ states that asphalt emulsions may be produced by using as emulsifier small proportions of alkali hydroxide or a silicate with an alkaline reaction. The asphalt emulsion obtained is mixed with sufficient tannic acid so that pH = 7, and then a soluble salt of a strong acid, such as ferrous sulfate, is added, bringing the pH to a value between 7 and 4.

Asphalt may be emulsified by using an emulsifying agent prepared by mixing 60-90 per cent of a petroleum distillate lubricating oil and 10-40 per cent of benzene, toluene, or diphenyl, heating the mixture with a sulfonating agent; water is added to the resulting material and the material allowed to stratify, separating the intermediate sludge-like layer therefrom and adding finally an excess of sodium hydroxide to the latter in order to neutralize the layer and to form sodium salts of the petroleum hydrocarbon-aromatic sulfonic acids.^{221a}

Paix and Cie¹⁰⁷ patented a process for increasing emulsification of bitumens difficult to emulsify by adding unsaturated rosin acids or

cyclic alcohols to the initial substances. Also, compressed air is blown through the mixture for 2 to 6 hours at a temperature of 210° to 250°.

Aqueous bitumen emulsions with a fine dispersion are obtained by treating coarse-grained bitumen emulsions obtained by using as emulsifying agents positively or negatively charged polysilicic acids or their salts, so that the electric charge on the particles of the emulsifying agent is increased to such an extent that their mutual repulsion causes splitting of the bitumen globules without any mechanical subdivision of the emulsion being necessary, *e.g.*, by heating. The silicic acids may be obtained by ripening colloidal clay suspensions (to which water has been added in the ratio of 1:3) for about 36 hours until suitable hydrates are formed. Asphalt, in the proportion of about 50-60 per cent of the emulsion, is then added to form a coarse-grained emulsion in which the colloidal particles have disappeared from the aqueous phase and settled on the bitumen particles. This emulsion is then heated for 1 to 3 hours at about 90° until the final emulsion is formed.^{4,5}

Aqueous emulsions of pitch, bitumen, and asphalt, in which the aqueous phase is the continuous phase, are prepared by dispersing the bitumen material in a hot, dilute solution of an alkali, for example, 0.5 per cent of potassium hydroxide, calculated on the amount of bituminous material used, and using as an emulsifier a proportion of fatty acid pitch and casein. The quantity of water in which the material is first dispersed and the proportion of the protein taken is such as to prevent the reversal of phases.

An aqueous dispersion of comparatively coarse bitumen particles is obtained⁶¹ when a thin stream of melted bitumen is led into a paste made of water and an emulsifier containing humic acid, until stirring of the mass formed becomes difficult. Then enough water is added so that the mass may be readily stirred when a new amount of bitumen is added; thus an emulsion is formed in which the bitumen content is about 50 per cent. This fluid dispersion system of the bitumen is claimed to have a high stability. Likewise, the bitumen and water may run together into the stirring container; but in this case the dilution must be such that after addition of the total amount of the bitumen the indicated concentration is reached.

A bitumen emulsion is produced by combining a bitumen with water-soluble substances, such as sodium chloride or glycerol, in sufficiently small amounts so that, when the material obtained is dispersed in water, there are produced within the dispersed particles osmotic pressures initially greater than those exhibited by the continuous phase, so that adsorption of water from the continuous phase into the disperse phase is effected.⁶⁹

The Flintkote Co.⁶⁸ reports an aqueous, highly concentrated bitumen dispersion obtained by adding melted asphalt to an asphalt dispersion with small bitumen particles, prepared as usual with soap in a colloid mill and stirring. It is claimed that the content of asphalt may be as high as 85 per cent. The bitumen dispersion obtained is liquid in a cold

state and its particles are 10 to 15 times larger than those of the initial dispersion.

A tar oil or petroleum asphalt may be readily emulsified with water by incorporating in it 0.5-30 per cent of its weight of finely divided brown coal low in humic acid and containing not more than 3 per cent of water.⁶² Bitumen emulsions suitable for subjection to low temperatures without breaking are obtained when a material such as Mexican petroleum asphalt is emulsified by the use of a rosin soap, such as sodium or potassium soap, which has been heat-treated for 2 hours at about 260-315° F. This heat treatment causes lowering of the viscosity number to 130 and below.⁸⁰

A bitumen emulsion which does not flow at high temperature and is plastic at low temperature is composed of 55 parts of bitumen, 10 parts of soap (comprising 40 per cent of resin or resinous oil and 60 per cent of a 7-per cent sodium hydroxide solution), about 30 parts of an alkaline clay paste (containing 15 per cent of bentonite, 78 per cent of water and 7 per cent of a 7-per cent sodium hydroxide solution), and 5 parts of a 35° Bé sodium silicate solution.¹⁸¹

An asphalt emulsion is prepared from 2 parts of asphalt emulsified in 1 part of water containing about 1.5 per cent of a salt such as sodium sulfite or sodium chromate having a neutral or basic reaction. It serves to reduce the interfacial tension between water and asphalt. As emulsifier is used about 1 per cent of triethanolamine oleate or a similar soap. The salt reduces the amount of soap required for the formation of a stable emulsion and imparts useful properties to it.²¹³

A bitumen emulsion is obtained from 60 per cent of bitumen containing 5-25 per cent of blown bitumen, water and small proportions (up to 2 per cent) of a stabilizing agent such as soap.³² Bitumen emulsions are obtained by suspending a powdered hard bitumen in an aqueous sodium hydroxide solution and adding it with stirring to a melted soft bitumen containing a saponifiable substance such as oleic acid.¹⁷⁷

Robinson and Sutherland¹⁸⁷ prepared bitumen emulsions by heating an aqueous alkali solution of lime, and of the carbonates or bicarbonates of the alkali metals, and mixing a saponifying material with the heated bitumen, which may contain naphthalene. A part of the calcium carbonate formed in the solution may be removed before the saponifying material is added. The amount of carbonate used must not be greater than that which will permit at least one-half of the available sodium or potassium to be liberated as sodium hydroxide or potassium hydroxide. Asphaltic or bitumen emulsions with a slightly acid reaction are formed by first forming a basic emulsion by means of sodium hydroxide or tribasic sodium phosphate and then adding sufficient citric acid or extracts of wood to bring the pH to a value of 6. Citric acid is added in two stages, of which the first is pretreated with sodium hydroxide. Small quantities of high molecular products, such as algin and/or casein, are recommended to be added to the basic emulsion before acidifying.¹⁶⁸

Highly concentrated aqueous asphalt emulsions may be prepared from an asphalt obtained from the residue of a tar oil heated to about 300°, into which water vapor is led, with increase in temperature to 325°; this serves to drive off 25-30 per cent of a thick, liquid oil, depending on its properties, leaving asphalt as the final product. This asphalt (about 50 g) is melted with 1-2 g of montan wax and 0.5-2.5 g of oleic acid at 120-130°. The mixture obtained is introduced in a fine stream into a dilute sodium hydroxide or soap solution with rapid stirring, and heated to 90°. A short boiling may improve the asphalt emulsion formed. The latter may be mixed with a rubber emulsion at 55° (not higher) without any protective colloid or stabilizer. Aluminum and mica or silica gel, which provide fire-proofing and better resistance qualities, may be added.

Painter, Moreton and Hill¹⁶⁶ patented a bitumen emulsion consisting of 36 gallons of asphalt mixed with a colloidal solution of 8 to 10 pounds of hydrous magnesium silicate (obtained from the Mohave desert) in 20 gallons of water and 250 to 420 cc of 0.1*N* acetic acid with additional water as desired (10 lbs).

Kirschbraun¹¹² patented the production of a complex emulsion system thinner in consistency and with a higher bitumen content than either constituency of a combined emulsion. An asphalt-clay emulsion as ordinarily produced is of a comparatively viscid consistency and, when mixed with a soap emulsion of asphalt or another bituminous base suitably proportioned, gives a system of a much thinner consistency and improved suspendibility, the asphalt or bitumen content being increased in relation to the amount of asphalt-clay emulsion present, despite the increased fluidity. Thus, with certain types of relatively non-suspendible stable emulsions of the mineral powder type, the resultant system is completely suspendible. In general, the asphalt-clay emulsion may be composed of 35-60 per cent of asphalt, 40 per cent of water, and a small amount of clay. The soap emulsion will ordinarily contain about 70 per cent of asphalt, 30 per cent of water, and a small amount of soap. All things considered, the character of the clay emulsion, the alkalinity of the soap emulsion, as well as other factors, determine the treatment applied, which consists in adjusting the hydrogen ion concentration by the addition of alkali to the clay emulsion, thereby increasing its pH value to approximately that of the soap emulsion.

van Westrum²⁴⁶ prepared a tar emulsion as a dust preventive liquid called "Westrumite." This emulsion was made from a semi-asphaltic crude oil and a large quantity of soap, but it was unstable and the asphalt coating dried out quickly. Westrumite had an asphalt content of about 30 per cent; commercial asphalt emulsions use topped crudes containing 70 to 80 per cent of asphalt, and emulsified asphalt paving cements, 70 per cent of asphalt and a small amount of soap. Asphalt-tar emulsions are prepared first by emulsifying asphalt in water, using an emulsifier, and then dispersing in it tar, which must have a density of not more than 1.15 at 25°. ¹⁵

Smith and Douthoff²⁰² prepared bitumen oil-in-water emulsions by dispersing asphalt in a finely divided state in an aqueous dispersing medium having an alkalinity slightly less than the critical alkalinity above which a water-in-oil emulsion would be formed from the same constituents. The difference in alkalinity may determine the type of the emulsion by controlling the relative percentage of antagonistic emulsifiers present.

Schmids Erben A.-G.^{195a} prepares a concentrated, well-spreading and fast-breaking fluid emulsion from a mixture of a tar emulsion and an asphalt emulsion.

Bitumen may be emulsified by mixing it, before dispersion, with water carried in a water-in-oil emulsion without the addition, prior to this mixing, of water-soluble substances either in the water-in-oil emulsion or separately. The oil used for the water-in-oil emulsion must be capable of dissolving the bitumen, and is preferably less viscous. It should be neutral so that it will not react with emulsifying agents used to obtain the aqueous dispersion. Paraffin is a suitable material, and oil and water is dispersed therein by a water-insoluble agent, such as aluminum stearate or oleate. Part of or substantially all the water is removed by evaporation after the bitumen has been mixed with the water-in-oil emulsion before dispersion in water. This treatment redistributes the water-soluble substances contained naturally in the bitumen, so that on dispersion in water they increase the water adsorption of the bitumen and hence its viscosity. Increase in viscosity is effected by better mixing of the bitumen with the water-in-oil emulsion.^{52a}

Foster Company^{71a} patented a preparation of a bitumen emulsion consisting of a suspension of colloidal clay (pH 4.8) as dispersion agent and a dispersed bitumen having a particle size 0.01-0.02 mm. The emulsion should contain about 10 per cent of clay, 50 per cent of bitumen, and 40 per cent of water.

The degree of dispersion of a bitumen emulsion varies as a function of the pH of the aqueous phase, and the maximum dispersion corresponds to a maximum stability; the stability is greatly affected by emulsifiers, *e.g.*, the stability of a Parmeo bitumen without an emulsifier or softener lies within the pH limits of 10.2 to 12.5. When the bitumen is emulsified with 0.9% of olein, the stability limit is within a pH range of 8.1 and 12.6. Viscosity and breaking point are also found to be affected by the pH. Control of viscosity by pH has some practical difficulties, and it is better to employ such materials as stearic acid or sulfonic acids. Certain salts that have the effect of partially neutralizing the electric charges on the bitumen globules may be used to influence the breaking of the emulsion.^{230a}

Flavigny,⁶⁶ discussing the possibilities of a mechanical subdivision of bitumens in preparing their emulsions, states that for the same bitumen dispersion with mixers is coarser than that produced with a homogenizer or a colloid mill. For the same disperser, the fineness of dispersion generally increases with the velocity of rotation.

Flavigny proved that the action of the emulsifier predominates over the influences exerted by the type of dispersion applied. He also found that the effect of the stabilizer may oppose the division of the bitumen and lead to the formation of coarse and irregular systems. An excess of emulsifier would result in coarse emulsions.

Lechler¹²⁴ prepared emulsions by mixing liquids in a spray nozzle in which the liquids are given a rotary motion. These liquids are so thoroughly and completely mixed that the material leaves the nozzle issues in a very fine spray.

Ferri^{65a} prepared gas-tar or natural-asphalt emulsions by heating the tar or asphalt to its melting point and mixing with an optional emulsifier. With steady stirring of the hot mixture, he added cold water until the emulsion formed contained about 50 per cent of water.

Gnadagni⁸⁴ described equipment in which tar is mixed with 2 to 5 per cent of a vegetable or animal fat and reacted at 100-150° in an aqueous alkali solution such as sodium hydroxide, sodium sulfite, or water glass, the soap thus formed acting as the emulsifier. The addition of about 5 per cent of a solvent for the tar, *e.g.*, tar oil or mineral oil, favors emulsification.

Emulgia Vertriebes. f. Asphalt, Teer und Strassenprodukte⁵⁸ heat tar above the critical point of the emulsifying liquid, permitting it to flow into the emulsifying liquid (previously warmed to 95-100°) at such a rate that the vapor formed causes the formation of a finely divided emulsion without the use of stirring equipment or special and large amounts of an emulsifier. The emulsion may be obtained in a concentrated gelatin-like state and be diluted without break-down. The addition of filling materials, such as sand, when spread over road surfaces, causes the emulsion to break readily.

Flintkote Co.⁶⁷ patented an emulsification process in which the emulsifier and the aqueous suspension of asphalt are led continuously in separated streams through a closed receiver in which a rotary stirrer is fixed.

Socony Vacuum Oil Co.²¹² describes an apparatus in which asphalt is emulsified in water with a small amount of soap. The equipment consists principally of a drum divided into two compartments. In the upper chamber the asphalt is mixed by a paddle stirrer with resin or a fatty acid, water being introduced in regulated amounts; the lower chamber contains the hot alkali solution.

Champion⁴¹ uses aqueous emulsions of bitumen or tar, hot and only slightly diluted with water. He, as well as Disney,⁴⁰ describe an apparatus used for emulsifying tars or bitumen.

The Comp. Ind. et Minière du Nord et des Alpes⁴⁴ describes a plant for the manufacture of tarry, bituminous and similar emulsions. This plant comprises a portable melting apparatus for the bitumen, a tank for mixing water and the emulsifying agent, an emulsifier, and a tank for storing the emulsion. The melting apparatus is heated by an inner furnace surrounded by an oil jacket, which is immersed in the bitumen.

The other auxiliary apparatus, emulsifier and heating tanks, are heated by means of pipes through which oil from the jacket is circulated.

The preparation of bitumen emulsions in a colloid mill with addition of soap may be improved, with respect to preventing foam formation caused by air being sucked in, by placing the mill in a heated bath of very viscous, heavy petroleum.¹⁷¹

Thalman²²² patented an apparatus for preparing emulsions of petroleum, asphalt and water and other materials. The mixing apparatus comprises a jacketed cylinder through which a shaft extends and on which discs and blades are mounted.

Concentric tubes may be used with success for a simultaneous introduction of the bitumen emulsion, an electrolyte solution serving to coagulate it.²⁷

Specific Methods for Stabilization of Asphalt Emulsions

Geigy A.-G.⁷⁶ recommends emulsification and stabilization by adding to the aqueous bitumen emulsions condensation products obtained by condensing formaldehyde with phenols or its derivatives, or substitution products. The condensation products are soluble in water or alkali and may be added to the bitumen before it is emulsified.

The International Bitumen Emulsions Corporation¹⁰³ patented bitumen emulsification and stabilization processes. Fibrous or mineral fillers are added when emulsions are prepared solely with alkaline water, using small amounts of sodium phosphate or, in the case of soap-stabilized emulsions, sodium phosphate with an alkaline-earth salt, such as calcium chloride, to increase its fluidity.

Thompson²²⁶ prepared emulsions in the usual manner; but, to make them stable to temperature changes, as well as to coagulation when mixed with sand, he added a small percentage of bile acids, for example, glycocholic and taurocholic acid in the form of their water-soluble salts. Other ingredients in the bile acids need not be removed.

For the purpose of preparing stable emulsions of bitumens, dispersing them with one part of the emulsifier determined for that particular emulsion and mixing the dispersion obtained with the remainder of the emulsifier is recommended.¹⁶

The coatings of bitumen-tone emulsions may be stabilized against water by adding to them suitable proportions of a fluorine silicate; 0.5-10 per cent of ammonium fluosilicate is suggested.¹⁴

Bitumen emulsions which break readily may be stabilized by mixing them with an alkali caseinate and an acid so that the emulsion has a pH value of about 8.5. Formaldehyde⁸ is added to the mass as protecting agent for the casein.

Relatively stable aqueous dispersions of bitumen materials are prepared by adding calcium resinate to the bitumen and dispersing it in a neutral or alkali solution of an alkali resin soap. The dispersions may be further stabilized by the addition of a solution of a normally coagu-

lating electrolyte, such as calcium chloride, in an amount equivalent to the amount of soap used.²⁶

Asphalt emulsions may be prepared by using as stabilizer a soap formed from a vegetable pitch, such as cottonseed oil residue. For example, 85-98 per cent of asphalt forming an emulsion on heating, should contain 15-20 per cent of stearin pitch and less than 2 per cent of alkali.³⁰

Stable tar emulsions are obtained from tar freed from naphthalene or its homologs and then brought to a state of an emulsion in an aqueous soap solution.⁸⁵ The properties of the bitumen emulsion may be improved by the addition of clay pastes containing alkali and silicates. Earths such as bentonite and wilkenite are suitable.¹³²

Bitumen dispersions, prepared in an aqueous solution of an alkali soap of solid resin containing a calcium or similar resinate, may be stabilized by adding a normally coagulating electrolyte solution in an amount equivalent to that of the alkali rosin soap used as emulsifier. For example, lime-hardened rosin is prepared by heating at 140° until it is homogeneous. After this has cooled, a mixture of solid rosin (furfural-extracted type) (100 parts) and hydrated lime (3.75 parts) is dissolved at 140° in an equal amount of fuel oil (viscosity 6000 sec. Redwood I), and 4 parts of this solution is added to 100 parts of 200-penetration bitumen. The mixture is then dispersed in a neutral 0.05N potassium rosinate solution to give a dispersion of 57 per cent bitumen content.⁷⁰

A bitumen emulsion stable to alternate freezing and thawing is obtained when a bitumen is dispersed in water, using as emulsifier 3-8 per cent of "B" resin soap with 10-20 per cent of unsaponifiable ingredients. The emulsion had a 0.1 to 0.5 per cent excess of free alkali.¹⁸⁹

Emulsions of materials such as asphalt or paraffin may be stabilized by the addition of saponified products of materials adsorbed upon spent fuller's earth used in filtering cracked petroleum vapors and removed from it by a suitable solvent such as acetone or benzene.²²⁰

The stability of bitumen emulsions containing a water-insoluble emulsifying agent, such as humic acid or insoluble emulsified lignic acid, is improved by adding a water-soluble salt not having an alkali reaction, such as sodium chloride, calcium chloride, or aluminum sulfate, in a proportion based on the total amount of the emulsion (not above 2 per cent). By pouring a melted bitumen into alkaline water, a readily breaking emulsion is prepared, which is stabilized when warm by the addition of an aqueous blood solution. The pH value of the emulsion should be above 9, and preferably between 10 and 11.¹⁰⁵

Stable bitumen emulsions are prepared by means of alkali substances and by addition of a high molecular substance with citric acid until an acid reaction is obtained.¹⁶⁴

Aqueous bitumen emulsions are prepared in the ordinary manner, using sodium hydroxide (2-3 per cent) as an emulsifier and turpentine oil (6-9 per cent) as a stabilizer.

A stable bitumen emulsion has been prepared from melted bitumen in an aqueous solution of an emulsifier which in itself forms an unstable emulsion, but may be stabilized by cooling to 100° F by the addition of an albumin, such as casein, or a carbohydrate, such as starch.²³²

Two bitumen emulsions, one comparatively stable and containing clay, and the other comparatively unstable and containing soap, may be mixed without precipitating the latter if, before mixing, the pH of the first emulsion has the same value as that of the second.¹⁷²

A stable bitumen emulsion is prepared by the addition of small amounts of water containing a soluble emulsifier, such as ammonium resin soap, to the bitumen. With further addition of water containing the emulsifier, the water-in-oil emulsion may be converted into the oil-in-water type.²²³

Yuzhilin²⁴⁹ proposed methods for forming tar emulsions and dehydrating them. He stated that the stability of tar-water emulsions increases with their coke dust content (beginning at 2 per cent of dust) and with decreasing size of dust particles. The difference in the specific gravity of water and tar in the existing liquids does not interfere with the formation of emulsions.

The tar emulsion from Tscheljabinsk coal could be decreased to 5-6 per cent water content by heating to 45°, and the Moscow generator tar could be readily dehydrated to 2.5 per cent by heating in an autoclave to 110°.

A method of producing a stable emulsion of coal tar and asphalt flux oil has been described by Barrett Co. (Fair, Jr.¹⁷). The disperse phase of the emulsion contains a predominant amount of coal tar. Fifteen parts of oleic acid are added to 250 parts of asphalt flux oil, heated to about 100°; then 750 parts of water containing 34 parts of aqueous ammonia are added. The emulsion of asphalt flux oil produced has a viscosity substantially greater than that of water. Thereafter, 1500 parts of coal tar (specific gravity 1.18 or more) containing 45 parts of oleic acid, are added, and the whole is heated to about 70°. The tar is vigorously agitated with the emulsion of asphalt flux oil. Finally, the mixed emulsion is subjected to intensive mechanical disintegration by passage through a colloid mill. The second patent relates to incorporating an additional emulsifying agent directly in the emulsion formed, thereby obtaining a more stable emulsion than if all the emulsifying agent were present during the dispersion of the tar.

Stable asphalt and bitumen emulsions are prepared by Ovregard¹⁶³ from an alkaline emulsion formed from sodium hydroxide or tribasic sodium phosphate by adding in two portions citric acid or extract of peat or certain woods, the former being sufficient to react with the alkali and the latter sufficient to raise the pH above 6.5. The action of the acid may be retarded by adding small proportions of high molecular compounds, *e.g.*, casein. The consistency of the emulsion may be adjusted by adding bivalent substances, such as calcium chloride or ferrous sulfate.

A comparatively stable emulsion of bitumen, water and an emulsifier, such as an asphalt-clay emulsion, and a relatively unstable emulsion, such as an asphalt-soap emulsion, are mixed after the pH of the former has been adjusted approximately to that of the latter. The emulsion obtained is one of intermediate stability and is claimed to be suitable for use in road making.¹¹³

Stable aqueous emulsions of road tars, pitch, bitumen, etc. are made by the Thermal Industrial and Chemical Research Co., Ltd.²²⁴ by preparing an inverted emulsion of the water-in-oil type from the whole of the tar; the quantity of water used is not less than 5 per cent of the tar, an ordinary emulsifying agent being added. This emulsion is added to and dispersed in a concentrated aqueous solution of an emulsifying agent containing not less than one-eighth part by weight of the emulsifying agent. The first emulsion is thereby converted into the oil-in-water type.

Barber Co., Inc. (Smith ^{14a}) patented the preparation of emulsions of the oil-in-water type by dispersing bitumen in the presence of clay in water. In order to render the film formed stable to water, metal salts are added. For example, bitumen, 45 per cent (preferably 50 per cent); bentonite, 2-10 per cent (preferably 7.5 per cent); water, 25-55 per cent (preferably 43.5 per cent).

Salts	Amount (%)	Salts	Amount (%)
$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	0.1-10	$\text{Cu}_2\text{I}_2\text{Br}_2$	2-10
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$		AgNO_3	
ZnCl_2	0.5-10	Ag_2SO_4	
$\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$	0.6-10	$\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$	0.5- 5
$\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$		PbCrO_4	0.5-10
ZnBr_2	1-10	$\text{TiF}_4 \cdot 2\text{H}_2\text{O}$	
ZnI_2		TiCl_3	
ZnF_2		$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	
$\text{Zn}_3(\text{PO}_4)_2$		SnI_4	
$\text{Zn}(\text{CN})_2$		SnSO_4	
ZnCO_3	4-10	$\text{Sn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$	
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	0.1-10	PbCl_2	1-10
CuBr_2	0.5-10	PbBr_2	
$\text{CuCr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$		PbI_2	
$\text{Cu}(\text{OH})_2$		$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$	
$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$	1-10	$\text{Pb}(\text{NO}_3)_2$	
$\text{CuF}_2 \cdot 2\text{H}_2\text{O}$		$\text{Sn}_2(\text{PO}_4)_3$	2-10
$\text{CuF}_2 \cdot 2\text{NH}_4\text{F} \cdot 2\text{H}_2\text{O}$		$2\text{SnO}_2 \cdot \text{P}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$	
CuCl_2		PbSO_4	5-10
$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$			
$\text{Cu}(\text{SCN})_2$			

Tar-water and asphalt-water emulsions are often used to protect construction materials against corrosion. Verona and Fostiropol ²³⁸ investigated emulsions from Pacura of a paraffinic and asphaltic nature. Alkali hydroxides in amounts of 0.05 to 10 per cent were used as emulsifiers. About 250 different combinations were prepared, and experiments indi-

cated that (1) the type of emulsion depends on the order of introduction of phases, of the percentage of phases, and the percentage of potassium hydroxide contained in the emulsions; (2) the particle size of the disperse phase varies within close limits; (3) the color of the emulsions depends on the materials originally used; (4) the stability of the emulsions depends on type, the percentage of tar or mixture of tar and asphalt, and viscosity; and (5) the viscosity increases with increase in the added phase, regardless of whether it is tar or water.

Smith²⁰⁰ states that the latest and most important development in emulsions is the stabilization of soil. This refers to soil characteristics in which the capillarity of the soil and its affinity for water are reduced to a point that insures the required bearing strength in the soil under actual conditions of exposure in the subgrade. Stabilization is effected by uniformly distributing minute particles of asphalt throughout the entire clay mass. In soil stabilization the soil is simply rendered resistant to water entering by capillarity, thereby retaining the bearing strength characteristic of the same soil in a dry, compact condition.

Fostiropol and Verona⁷² found that, on mixing an aqueous emulsion of an oil with a sufficient amount of powdered calcium oxide, hydration of this compound results in conversion of the total mass to an extremely fine, homogeneous powder. As a matter of fact, the state of dispersion of the three elements (water, oil, and calcium oxide) permits an intimate reaction on a vast contact surface. The calcium hydroxide, which is formed with development of heat and an increase in volume, adsorbs all the oily particles. This phenomenon has been studied for emulsions made of mazout of an asphaltic, as well as a paraffinic, nature. The results obtained for both were practically the same, the only difference being that the latter required a slightly larger proportion of calcium oxide. Asphalt emulsions of the water-in-oil type are, in general, very thick, their mixture with calcium oxide being resolved with difficulty. These emulsions may be made more fluid by heating if, in every case, the 35° limit is not exceeded. The stability of asphalt emulsions of the oil-in-water type is reduced in the presence of calcium oxide; therefore, to obtain a homogeneous mixture, it is necessary to stabilize them.

In connection with the work of Fostiropol and Verona, it is interesting to note that calcium oxide powder and calcium naphthenate act as catalysts in the oxidation of asphalt. Kapatzinsky^{108a} stated that when 12 liters of air per minute are passed through a kilogram of oil goudron at 300°, both catalysts act as accelerators, calcium naphthenate giving the best results. In large-scale production, calcium naphthenate has no accelerating effect. This is attributed to the physical conditions under which the reaction takes place, namely, as a result of an increase in temperature the amount of air introduced must necessarily be decreased and, in addition, the heat originating by the exothermic reaction must be dissipated.

Foulon,^{70a} discussing the preparation of simple and poly- emulsions from bitumen, tar, and mineral oils, states that sludge, soaps, and resins

act as stabilizing substances, whereas castor oil and chlorinated high molecular hydrocarbons increase the viscosity of mineral oils. Emulsifiable oils or aqueous emulsions from mineral oils are obtained by using oil-soluble mineral oil sulfonates, ethanol, amines, and similar agents.

Finely divided fillers with the application of colloidal lime, bentonite, and similar colloids, as well as a small percentage of a suitable electrolyte, such as sodium carbonate, are dispersed in water and then mixed with the bitumen emulsion.^{204a}

Lewis⁶⁰ claims that bitumen-water dispersions can be prepared by using as a dispersing agent a material of definite characteristics, such as: (1) ability to be "wetted" by either the dispersion medium (such as water), or the material dispersed (asphalt); (2) preference for the dispersion medium when previously wetted by it in the presence of both the dispersion medium and the material to be dispersed; (3) readily dehydrated; (4) non-hygroscopic; and (5), insoluble and inert with respect to ordinary reagent. Aluminum hydrate, preferably in a gelatinous state, proved to be very efficient for the dispersion of asphalt in water, was thoroughly wetted by it, and did not mix with the bodies of the asphalt particles; when the dispersion was dried, the aluminum hydrate adhered tenaciously to the asphalt around it and was not wetted thereafter by water. An aluminum hydrate paste together with asbestine also has been proposed as a dispersing agent. Thus a dispersion of bitumen in water may comprise 80 per cent of bitumen, 10 per cent of aluminum hydrate paste, and about 10 per cent of asbestine, with sufficient water to maintain the dispersion.

Preparation of Bitumen Emulsions for Road Construction

Deutsche Vialite G.m.b.H.⁴⁸ patented coarse dispersions of bitumen for road surfacing, prepared by using pitchy products from the evaporation of sulfite liquor as dispersion agent and stirring with water at about 90°.

Bojanowski³⁵ produced tar emulsions for construction and maintenance work by homogenization of coal-tar, or its stabilization with a 1:1 mixture of the following emulsifying agents (1a and 1b or 2a and 2b): (1a) soap, pitch, or casein (naphthenic acid) in an aqueous solution up to one per cent of the total; (1b) certain chloro- derivatives of aromatic compounds in water glass up to 3 per cent of the total; (2a) saturated aqueous solutions of humic acid obtained by the oxidation of coal and certain chloro- derivatives of aromatic compounds; and (2b) water glass up to 3 per cent of the total.

Plauson¹⁷⁶ recommended mixing water with the liquid bitumen, such as melted asphalt or tar, and subjecting the mass to pressure, after which it is mixed to form an unstable emulsion, and then sprayed on the road surface. This is a continuous operation.

Mineral-oil residues, resulting from the distillation of mineral oils in

the presence of alkalis, contain considerable proportions of alkali naphthenates soluble in water. These bitumens may be made applicable for road construction purposes if they are emulsified with mineral fillers or mixed with cement and treated with a calcium chloride solution; the soluble alkali naphthenates are thus converted into the insoluble calcium naphthenates.²⁵

Bitumens may be emulsified into road construction material by means of an emulsifier consisting of a mixture of 10 parts of aluminum oxide or some other aluminum salt; one part of petroleum oil, and one part of water. If tars, instead of petroleum oil, are emulsified, oils containing anthracene are used.³³

A mixture of artificial or natural asphalt combined with powdered marble has been proposed as a preparation for bitumen road material.³⁹

Treatment of lubricating-oil fractions with solvents, such as furfural, gives extracts which, when mixed with asphalt or mineral-oil residues, act as binding agents. Before using, the hot mixture is treated with air or oxygen-containing gases.^{79a}

An asphalt emulsion for use as a pavement binder is obtained when an emulsion of a soft, solid bitumen, such as soft asphalt, is incorporated in a hard asphalt emulsion. This soft asphalt is fusible with the hard asphalt, and fusion is prevented by the dispersing film formed in the interface, which hinders coalescence until the emulsion is dry or has been broken.

Material for road construction may be prepared by mixing heated gravel with broken pieces of a viscous bitumen from Kentucky. Shortly before the bitumen starts to boil, an asphalt cement is added to the mass.⁷³

A road construction mass is obtained¹⁰⁵ from a colloidal dispersion of an earth, such as clay or the like, in water to which a small amount of bitumen in the form of an aqueous emulsion is added. The amount of bitumen should be so small that no binding takes place. The mass, after drying and solidifying, repels water.

An emulsion for use in street construction, according to Labourse's patent,¹¹⁸ consists of a mixture of 500 kg of tar or bitumen, 500 kg of water, 10 kg of calcium hydroxide, 2 kg of aluminum sulfate and 5 kg of sulfur melted together with the bitumen, after which 2 kg of sodium carbonate and 50-150 kg of a substance such as slate flour or kaolin is added.

Bitumen emulsions suitable for impregnating purposes and street construction are obtained from asphalt, tar, or resins, as well as bitumen-like masses, by dispersing them in a hot alkali solution with the addition of a protective colloid at about 100°; an alkali casein solution and fatty-acid distillation residues are suitable as emulsifiers.¹⁴⁷

Emulsions for road work are obtained by melting a bitumen, such as "Spramex," and emulsifying it with a previously formed emulsion of a neutral glyceride, such as bone fat or fish oil, in an excess of alkali carbonate solution.¹⁷⁴

A sulfonated fatty oil is recommended as an emulsifying agent for bitumen emulsions to be used in preparing road-construction material. The latter are covered with a liquid mixture composed of a volatile oil (Diesel oil, coal-tar distillate), the sulfonated fatty oil, and the bituminous binding material.¹⁷⁷

A chemically active asphalt, which separates readily from filling material, is prepared by heating asphalt with sludge in vacuum, washing, and drying at 180°.¹⁷³

Bitumen emulsions for street or like construction are made from a bitumen treated with a hydroxide of an alkaline earth. By neutralizing the acids contained in the bitumen, soaps soluble in oil but insoluble in water are formed. On heating the mass obtained to 400-600° F, these soaps decompose, forming ketones soluble in oil. This ketone-containing bitumen is then emulsified in the ordinary manner with alkaline water prepared from an alkali soap of a fatty acid.¹⁸²

An asphalt emulsion for coating purposes is prepared by incorporating in an aqueous emulsion of asphalt containing china clay as an emulsifier (or, if desired, fibrous material like asbestos or cotton) a 0.5 per cent lead sulfide concentrate, or its equivalent in red lead oxide or lead monoxide, as a rust inhibitor.¹⁹⁵

A paving material composed of gravel coated with hot bitumen, cement and bitumen emulsion and solidified by pressing has been patented by Tomasello.²²⁸

Bitumen emulsions for street construction are prepared by mixing a fraction of crude mineral oil containing saponifiable substances with an aqueous alkali solution, whereby an oil-in-water emulsion is formed. The latter is then mixed with melted asphalt which in itself cannot be emulsified with an alkali solution but which, in this case, is emulsified.^{234a}

Emulsions for road covering are prepared by emulsifying the warm bitumen, such as asphalt, in water in the presence of suitable emulsifiers and with the addition of suitable stabilizers. This method readily induces emulsification, and when the temperature drops to 40°, one or more volatile agents, such as petroleum or tar oil, are added, and the process is completed.^{45a}

A construction mass is obtained from heated gravel coated with hot asphalt. The substances are heated in a mixer with water containing the dissolved emulsifier, for example, 0.5 per cent of sodium hydroxide, and the water is partially evaporated so that a thin layer of water may be formed on the bitumen-coated gravel.²³⁴

Self-emulsifiable asphalts are obtained by distilling an asphalt-containing petroleum crude oil up to 400° F. and then mixing the residual oil under a suitable pressure with a low-boiling solvent, such as ethane, propane, or butane at about 250° F. Asphalt is precipitated and separated from the oil and solvent. Excess solvent is stripped with natural gas or steam up to 400° F. The hydrocarbon solvent may be mixed with phenol, cresol, phenylamine, or furfural. Variation in the amount of solvent, and temperature of precipitation effect changes in the softening

points of the asphalts. Asphaltic emulsions may be prepared (1) as quick-setting and (2) as slow-breaking in the following manner: (1) 20 per cent of solvent-precipitated asphalt obtained by reducing a Venezuela crude oil up to 400° F is blended with 80 per cent of asphalt, fire-reduced at 620-650° F; 55 parts of this mixture are heated and added to 44.8 parts of hot water containing sodium hydroxide (0.13 part) and bentonite (0.07 part). (2) A slower breaking emulsion is obtained by blending 60 per cent of solvent-precipitated asphalt with 40 per cent of asphalt reduced up to 650° F; 52 parts of this mixture are added to a solution of 0.15 part of sodium hydroxide in 47.85 parts of water.^{210b}

Colored bitumen emulsions are obtained by mixing coal-tar pitch or other bitumens and coloring organic matter with water in the presence of blue clay.²⁴⁰

For road surfacing, the use of colored bitumen emulsion is recommended. This is prepared by incorporating a bitumen emulsion with an aqueous emulsion containing a pigment in which the emulsifying agent is an alkali, together with resin and pitch or resin and bone fat.²¹⁹

Treating bitumens in a definite manner before they solidify on surfaces is recommended. A mixture consisting of 2 parts of bitumen emulsion, 1 part of cement, and 8 parts of gravel is covered with dry cement and small irregularly formed metal pieces and then pressed into the bitumen support.

For road construction, foundation building, and roof laying, the material is applied in layers, the upper layer consisting of an aggregate of various sizes and cement in proportion to form interstices which are partly filled with stone chips, gravel, or sand, as well as with bitumen, tar, or similar substances in the form of an emulsion; the lower layer is composed of dense concrete, some of the aggregate of which interlocks with the aggregate of the upper layer.⁸¹

Haller⁸⁷ discusses an increase in the use of mixed emulsions for road building. He gives a table showing the properties of typical earths mixed with asphalt emulsions and also one illustrating the method of calculating the amounts of stabilizer which must be added to the emulsion for various grades of earth. He deduces a formula which relates percentage of stabilizer to particle size of that portion of the earth used which passes through a 200-mesh sieve.

Stability of Bitumen Emulsions Used in Road Construction

As has been indicated, there are many ways in which to prepare asphalt emulsions; and emulsions differ in their degree of stability, depending to a certain extent on the kind of emulsifying agent employed. The general rule that the finer the dispersion the greater the stability is also true of asphalt emulsions, but it has been observed that particle size in these emulsions usually ranges from 1 to 10 μ in diameter. Levi,¹²⁷ studying the size distribution of particles in an emulsion of bitumen in water, found that it follows a typical Maxwell distribution curve, with

a maximum on the curve at 2-3 μ . The sedimentation of emulsions depends upon particle size, gravity differential, and viscosity, as indicated by Stokes' law:

$$U = \frac{2}{9} \frac{r^2(\sigma - \sigma_w)g}{\eta}$$

where U is the settling velocity; r , the radius; σ , specific gravity of the asphalt; σ_w , specific gravity of the water and η , the viscosity of the continuous phase. Coarse emulsions, according to this law, will settle more readily than fine emulsions. On the other hand, an increase in the specific gravity of the continuous phase caused by dissolving salts in it, or an increase in its viscosity caused by dissolving salts or organic substances, will cause a decrease in the settling velocity, U .

In the case of emulsions, the transition to the unstable state is dependent on the settling velocity. The coagulation or merging of small individual globules into a continuous phase leads to resolution or breaking of the emulsions. After the globules have settled, an aggregation or clumping together of individual particles to form complex particles takes place, and this is what characterizes the phenomenon of "sludging." The sludging and the breaking of emulsions are two separate phenomena which, to a certain extent at least, are governed by different properties.²³⁹

The problem of breaking asphalt, bitumen, or tar emulsions is of great importance, because the practical application of emulsions is based on the process of breaking them gradually. When the breaking occurs on the surface on which an emulsion is spread, the disperse phase must adhere to this surface.

In studying the strength of the adsorbed layer of the emulsifying agent, Medvedkow and Sukhina^{142a} ascertain that bitumen emulsions are more stable at low temperatures than at high because of the decrease in the strength of the adsorbed layer of the emulsifier on the bitumen at high temperatures. The use of bitumen at high temperature lowers the quality of the emulsion because of the interaction between the bitumen and the emulsifier of the soap. An investigation of the effect of sodium hydroxide, sodium chloride, potassium chloride, calcium chloride, calcium sulfate, magnesium sulfate, ferric chloride, and barium chloride on bitumen emulsions indicates that univalent ions, when used up to a certain point, improve them, whereas other ions cause their partial or complete destruction.

In the case of road construction, the surface is made up of various substances, such as stone, sand, etc., and contact with these materials affects the emulsion system by changes in the electric charge, in the interfacial tension, and in the displacement of the emulsifier adsorbed in the interfaces. As a result of these changes, the bitumen coagulates, the water is expelled and, although molten bitumen adheres very poorly to the moistened surfaces of mineral substances,²⁰⁷ coagulated bitumen not only adheres to the solid surfaces, but binds them together. According to Nellensteyn,¹⁵⁹ interfacial tension seems to be the most important

factor affecting the stability of asphaltic bitumen solutions. The interfacial tension may be calculated with some restrictions from Antonow's¹⁰ rule: "The interfacial tension is the difference in surface tensions of the two phases." From this Nellensteyn concluded that the flocculation of an asphaltic bitumen solution occurs when the flocculating agent has a low surface tension and the asphaltic micelles have a high surface tension. It was further assumed that various liquids, according to their surface tension, may be subdivided into flocculating or peptizing reagents. In Table 2 are indicated flocculating reagents with low surface tension and peptizing agents with high surface tension.

Table 2

Type	σ 20° (dyne/cm)
Flocculating Reagents:	
Ether	17.1
Benzene, 40°-60°	17.4
<i>n</i> -Hexane	17.4
Ethyl acetate	22.9
Acetone	23.1
Butanone	23.6
Intermediate Zone:	
Carbon tetrachloride	25.7
Cyclohexane	26.0
Peptizing Agents:	
Chloroform	26.9
Benzene	28.8
Carbon disulfide	31.0
Pyridine	35.5

Nellensteyn mentions few surface-tension determinations of asphaltic bitumen at temperatures ranging from 180 to 200°, namely, 23.1 to 25.2 dyne/cm. At room temperature, they are above 30.0 dyne/cm, and therefore are not in agreement with the critical surface tension of 25.0 to 26.0 dyne/cm marking the boundary between the peptizing and flocculating reagents. This indicates that the asphaltic bitumen system is stable. Asphaltic bitumens vary little in their surface, indicating that the same liquids may be used either to peptize or to flocculate them. The only difference between the precipitates from dilute ethanol or acetone and those from benzene is that the former give a "soft asphalt," the latter a "hard asphalt." This difference is not caused by their chemical nature. It does not mean that a lower or higher degree of polymerization of the bitumen influences the degree of solubility, but that interfacial tension and miscibility determine the nature of the precipitate.

Regarding natural asphalt emulsions Dodd,⁵⁰ in his article "On the Resolution of Petroleum Emulsions," indicates that the nature of the asphalt solution in crude oil is probably dependent on the ratio of light fractions to lubricating fractions. As dispersion of the asphalt approaches that of a true solution, the tendency to emulsify should be expected to decrease. When diluted with gasoline, the emulsion becomes more stable and more difficult to break, indicating that the degree of dispersion in asphalt is more favorable to emulsification in light than in heavy frac-

tions. Skalmowski¹⁹⁸ emphasized the fact that certain materials, such as alumina, in the presence of water may have a destructive influence on bituminous substances used for street paving.

Two conditions are required of a bitumen emulsion for practical application: stability and the ability to resist complete breaking over a long period of time. This applies to the emulsion before use and not after it is placed on a road. If the material hardens too rapidly, spreading of the emulsion on the treated surface will be hindered. In another road construction method, namely, the penetration method,^{*} rather rapid coagulation of an emulsion is required to prevent the unbroken emulsion from diffusing into the foundation instead of spreading on the surface. Asphalt emulsions are also used in certain mixing processes in which an alkali solution precoats the surface to retard coagulation.¹⁵⁹

A further development of methods applicable to asphalt emulsification is necessary to simplify the process and to improve the quality of the asphalt bitumen in its practical application. With respect to processes of mixing, the literature indicates that two kinds of processes must be differentiated: hot and cold mixing. A systematic study of the subject is necessary to improve this industry. Perhaps it is advisable to pursue research in coagulation, since the practicability of asphalt bitumen is dependent on this property. A study of pretreated surfaces on which an emulsion is to be laid may also be recommended. The literature is barren on these topics. In all probability it may be logical to consider both the material to be spread and the physico-chemical properties of the surface upon which it is to be laid, namely, the interfacial tension as well as the spreading coefficient of the surfaces coated.

Agthe³ considered it important to pretreat the surface to secure good adherence of the bituminous coating; the surface is covered with a high-boiling oil, for example, a tar oil, thickened by dissolution in it of pitch, asphalt, and resin. The oil may also be applied as an emulsion, or small amounts of water-soluble soaps may be added to it.

Weber's²⁴⁴ researches seem to indicate that the breaking of asphalt bitumen emulsions is due to the withdrawal of water by capillary penetration into the stone mass. It is dependent on the amount of emulsifying agent in the emulsion, whether present as free alkali, alkali carbonate, or soap. The pretreatment of gravel with alkali renders the most active stones completely passive even to the most unstable emulsions. Soap is less effective than alkali in this respect. Washing an alkali-pretreated gravel with water does not restore its activity.

Reiner¹⁷⁸ improved the adherence and binding power of tar or bitumen emulsions (neutral or not alkaline) by adding a dispersion or solution of rubber in carbolic acid or its homologs. After the surface is covered with the rubber-containing bitumen emulsion, the alkali solution is sprayed. To increase the adherence of bituminous masses to gravel, a small amount of heavy-metal or alkaline earth phenolate may be added.^{207a}

For street paving, Léauté¹²¹ recommends the use of binding materials

whose viscosity increases to a considerable extent and which age rapidly, thereby preventing the phenomenon of "sweating" on bituminous streets, considered by this investigator as due to the capillarity of tars and bitumens. Particles of mineral additions lying close to one another act as capillaries, within which the tar or bitumen is raised, accumulating on the dry surface.

Bitumen emulsions which break readily are prepared from melted bitumen and an aqueous solution of sodium hydroxide. For the purpose of stabilization, the emulsion is mixed in a centrifugal pump with an alkali salt, such as sodium carbonate, sodium sulfate, sodium cresolate, or the like.²³³ The addition of blood freed from cells and maintained at a pH of 9 may be added to bitumen emulsions which usually break readily.

Nasini, Rossi and Baliau¹⁵³ studied the stability of bitumen emulsions with respect to metallic surfaces, and found that no bitumen is deposited on tin, silver, or copper surfaces, but that an equal amount of bitumen is deposited on aluminum, iron, zinc, lead, and nickel surfaces. The coagulating power of the ions of these metals on the same emulsions, and the potentials of the various metals when in contact with the emulsion were subjects for investigation.

Nasini and Rossi¹⁵² investigated the breaking of bitumen emulsions when in contact with solid substances, such as limestone, porphyry, pyrite, serpentine, active charcoal with varying ash content, and chlorine-free silicon oxide gel, as well as the adsorption of methylene blue and sodium carbonate, and found in most cases that the decomposition values are parallel with those of adsorption. Therefore, it is believed that decomposition occurs in the proximity of the solid surface and is simultaneously influenced by adsorption and the electrolyte given off by the solid substance. In general, it appears that, if the breaking of the aqueous emulsions is weak, the influence of adsorption predominates.

The treatment of bitumen emulsions may be carried out by using either method (A) or (B). In method (A) a small percentage of an alkali salt of an amphoteric element, such as sodium aluminate, sodium zincate, or sodium plumbate, is added to an aqueous bitumen emulsion; this salt decomposes on atmospheric exposure of the emulsion, yielding aluminum hydroxide, which accelerates coagulation of the emulsion. In method (B) the emulsion is treated with a small proportion of a volatile alkali reagent and a potential coagulant, such as an ammonia solution of cupric hydroxide, ammonium naphthenate, etc., so that, on atmospheric exposure of a film of the emulsion, the alkali evaporates and the whole emulsion coagulates.¹⁶⁸

Analyses of and Tests for Asphalt-Bitumen Emulsions

Certain methods have been adopted in practice for determining the various characteristics of asphalt emulsions which are important in their application. In general, the methods employed in different lab-

oratories for the analysis of these emulsions are concerned with (1) water content; (2) asphalt content; (3) emulsifying agent; (4) total alkali; and (5) free alkali. Additional properties of asphalt emulsions formed by various emulsification methods are specific with regard to their suitability in a variety of applications. A number of tests are recommended to determine the behavior of asphalt emulsions under the influence of various factors which alter these systems. Specifications for bitumen road emulsions require tests for stability, coagulation, sedimentation, demulsibility, binding power, homogeneity of dispersion, and many others.

Methods Employed in the Analysis of Asphalt Emulsions

Water Content. The xylene or McKesson method.¹⁴¹ The water is determined by distilling a xylene solution to which barium chloride has been added. To avoid errors due to condensation of moisture from the air, a modified Winkler-Jacques apparatus is used, whereby contact with the air is made through calcium chloride. Specifications fix the bitumen content at least at 50 per cent, the exact figures being guaranteed to one per cent.

Asphalt-Bitumen Content. Marcusson's method.¹³⁸ The emulsion is extracted with alcohol to remove both water and emulsifier, the bitumen filtered off in a Gooch crucible, dissolved in benzene, and an aliquot portion evaporated to constant weight.

Determination of the bitumen content in mixtures of coal tar and pitch may be made by measuring the dielectric constant. Derivatives of mineral coal and crude oil, especially their distillation residues, have different dielectric constants; therefore, by determining them in mixtures, the composition may be found. Measurements are taken either in the unchanged or in the dissolved state.^{240a}

Emulsifying Agent. Marcusson's method.¹³⁸ The alcohol is distilled from the above alcoholic extract, which is then dried at 110° and weighed. If the emulsifier is insoluble in both alcohol and benzene, it remains as a precipitate in the Gooch crucible, from which it is removed, dried, and weighed. Neubronner's method described by Weiss²⁴⁵ is considered more accurate. Emulsions should be tested for alkalinity, and normal samples should show an alkaline reaction.

Total Alkali is determined by thoroughly agitating and centrifuging a mixture of 20 ml of emulsion, 20 ml of chloroform, 30 ml of water, and an excess of normal sulfuric acid. Twenty-five ml of the clear aqueous layer are titrated for excess acid.

Free Alkali is determined by treating the aqueous layer, after resolution of the emulsion, namely, separating the soap from 20 ml by the addition of 30 ml of saturated salt solution, adding 10 ml of distilled water, agitating, and centrifuging. The aqueous layer is titrated with 0.1*N* acid for free alkali and carbonate.

Various Tests for Asphalt-Bitumen Emulsions

Softening Point.—Many tests are available whereby characteristics of asphalt-bitumens and their emulsions may be determined. The "softening point," which must be taken into consideration in relation to the conditions under which the bitumen is to be used, indicates the temperature at which it will soften and begin to flow freely. In the brass ring and steel ball method (I.P.T. Method A 20 and A.S.T.M. E 28-36T), determination of the softening point is carried out as follows: The ring is filled with the bitumen and immersed in water contained in a beaker, along with the ball. The ball is placed in the center of the upper surface of the bitumen in the ring under ordinary temperature conditions. The temperature is raised at a specified rate. When the softening point is approached, the ball begins to sink into the bitumen, tending to fall through the ring. The temperature at which the ball has fallen through a distance of one inch is recorded as the "softening point."

Penetration.—Penetration of residue is a means for determining the penetration of the asphalt originally used. A specific penetration of residue is a definite characteristic for certain classes of work. Usually the harder penetrations are used in well-graded mixtures containing fine or fine and coarse aggregate, whereas the softer penetrations are used for materials mixed on the job. A penetration of 60 to 100 is permissible for surfacing courses, and a penetration of 100 to 200 is permissible for materials mixed on the job, or premixtures of open structure. Open mixtures require an adhesive asphalt which will not become brittle in cold weather, yet remain sufficiently soft to permit further movement and interlocking of particles under traffic at normal temperatures, for stability in such mixtures depends upon the keying action.

The penetration test consists in pouring the bitumen into a penetration tin brought exactly to 25° and bringing the needle into contact with the surface of the bitumen. The needle is allowed to fall freely into the bitumen for five seconds. The extent of penetration is recorded with accuracy in hundredths of a centimeter. A metronome is used for timing the penetration. The penetrometer figure corresponds to the distance the needle penetrates the bitumen sample at 25° during 5 seconds under a load of 100 g (in this case 20 mm). The penetration test is also a measure of the consistency of the bitumen (I.P.T. Method A 18 A.S.T.M. D 5-25).

Ductility.—Harder asphalt may be used in denser mixtures. Ductility is used as a means of measuring adhesiveness. The ductility for the asphalt residue of an emulsion should not be greater than that required in standard specifications for asphalt itself. The same pertains to the specific gravity of an asphalt residue of an emulsion. Solubility is a means of determining the amount of materials, other than bitumen, incorporated in an emulsion, such as clays and inorganic substances.

The distance stretched without rupture is indicative of ductility.

According to I.P.T. Method A 19 A.S.T.M. D 113-35, the bitumen to be tested is poured into standard molds, and mounted under water at 25° in the testing machine. The sides of the molds are detached and then stretched mechanically at the rate of 5 cm per minute, or until the bitumen thread formed is broken.

Tests on asphalt emulsions include distillation, viscosity, settling, demulsibility, and coating.

Distillation.—The distillation test shows the percentage of light oil and water in the emulsion. A soft asphalt will have as high as 3.5 per cent of light oils as determined by oven test for five hours at 325° F. It is permissible for emulsions which contain soft asphalts to show certain percentages of oil distillate. The percentage of asphalt content has a direct bearing upon the fluidity of an emulsion.

Viscosity.—Such properties as viscosity¹⁶² of asphalt emulsions should be determined. Viscosity is determined with the Engler viscometer at 20°, or by modification of the Geissler pipette. In general, an accuracy of $\frac{1}{2}$ ° E in the range 2-10° E is obtainable. Emulsions for surface dressing should have a higher viscosity than those for penetration. For the former type, it is suggested that the English specification for the upper limit of viscosity is too low (4-15°).

The test for viscosity of emulsions containing fluxed asphaltic bitumen has been carried out with satisfactory accuracy by the Danish Government Laboratory of Road Research by means of a pipette. The experiments, in which capillary pipettes were employed, showed that this was possible with an accuracy of $\pm \frac{1}{2}$ Engler degree when the viscosity lies between 2 and 10 Engler degrees. The usual testing of viscosity of an emulsion by means of the Engler apparatus is a rather tedious procedure; that is why it was thought possible to replace it by the above method.¹⁸⁵

Malette¹³⁶ describes a viscosity test controlling bitumen emulsions.

Birger and Dahlberg^{33a} proposed identifying bituminous binding agents by viscosity measured in absolute units (centipoise, centistoke), using the penetrometer for low-temperature measurements and the viscometer for high-temperature measurements.

Sedimentation.—The settling test indicates the stability of an emulsion and is dependent upon fineness of particles, the gravity of the asphalt, and the amount of other substances, such as a bentonite, which are included in an emulsion to prevent settling. In many instances, the ultimate stability is not dependent on settling.

There are two principal methods for determining sedimentation characteristics. In the sieve test, both 100- and 200-mesh sieves are used; but an emulsion which shows no residue on a 100-mesh sieve will be satisfactory in practice, since it easily passes through the spray nozzle. In this method of sedimentation, the bitumen is determined after a definite time of settling. The second method consists in determining the bitumen (or water) in the bottom layer. An American modification method compares the bitumen contents of the top and bottom layers. Attempts

have been made to devise more rapid methods, as the settling tests may take three months.

Meunier and Mathieu¹⁴⁴ originally suggested the use of a centrifuge. Twenty ml of the emulsion without dilution was centrifuged at 2500 r.p.m., the upper layer measured and the lower layer sieved (0.2-mm mesh) and then washed with a 2-per cent soap solution. Although the centrifuge method gives satisfactory results comparable with those of the normal settling tests, the method is not suitable for general application.¹⁵⁴ Sedimentation tests are usually carried out by placing 250 ml of the emulsion in a narrow cylinder and leaving for six weeks (in the rapid method, eight days); any deposit obtained during this period must be redispersed in the emulsion on agitation.

Nasini and Rossi,^{152a} studying the sedimentation of concentrated (about 50 per cent) emulsions of bitumen, concluded that Perrin's law is not in order. Actually three layers are formed, namely, a top layer practically free from bitumen; a middle layer with a concentration of bitumen in the disperse phase corresponding to that of the original emulsion, and a bottom layer with a bitumen content up to 60-70 per cent. The analytical method used is based either on direct reading of the aqueous layer, or determining the bitumen content of the various layers.

Demulsibility.—The demulsibility test is one of the means employed to differentiate quick-breaking from other types of emulsions. A given quantity of 0.02*N* calcium chloride is added to an emulsion and the amount of asphalt recovered after draining the emulsion over a fine screen constitutes the percentage of emulsion demulsified or broken. Ordinarily, soluble soaps are used in emulsions, for calcium forms an insoluble soap with consequent coalescence of bitumen particles. If substitutes which dissolve the calcium soap are used, or if sufficient soap is present to adsorb the calcium chloride, the demulsibility is correspondingly low.

In reviewing the demulsibility tests which have been generally adapted in the United States, McKesson¹⁴² lists the following: (1) The demulsibility test (Myers) for quick-setting (penetrating) emulsions is made with 100 g of emulsion and 35 ml of 0.02*N* calcium chloride solution. To insure quick setting on the road, and freedom from damage from traffic and rainfall, the percentage demulsifiable should approach 100 as closely as possible. (2) The demulsibility test (Myers) for slow-setting (mixed) emulsions is made with 100 g of emulsion and 50 ml of 0.1*N* calcium chloride solution. To insure proper mixing time and proper coating, the demulsibility should not be more than 30 per cent when coarse aggregate is to be used, and not more than 5 per cent when fine, dusty aggregate is to be used. (3) A settling test is necessary to secure a properly prepared emulsified asphalt which will meet the demulsibility requirements and yet remain homogeneous and free from sediment in storage.

It has been proved by various experiments that when an emulsion is diluted with water containing calcium chloride it is possible to ascertain

whether it is of a "quick-breaking" or a "slow-breaking" type, and particularly whether the emulsion is "mixable." Mixed or slow-setting emulsions are prepared from emulsions which mix with rock, sand, or clay aggregates. The kind of road built with these types of emulsions may be classified as (a) retread; (2) cold premix; and (3) hot premix.

Stability Tests are differentiated as follows:

(1) Dilution with water containing calcium oxide. Water of 17° hardness (German) is added to the emulsion until coagulation occurs, the amount required being an indication of the type. By adding water containing lime, it is possible to determine whether an emulsion is of a "quick-breaking" or a "slow-breaking" type.

(2) Separation of asphaltic bitumen emulsions is accomplished by (a) adsorption on pumice stone; (b) evaporation, *i.e.*, loss of water on heating; and (c) extraction of water with alcohol, using Marcusson's method.

(3) Determination of the emulsifying agent by filtering off the liquid phase of the emulsion. The solid matter in the water removed or in an alcoholic extract is determined, but the former method is inaccurate with casein emulsifiers.

(4) Stability to cold is investigated by using a 50-ml stoppered cylinder as a container and passing the emulsion after one hour through a sieve at 8° C.¹¹⁴ As stated by Weiss,¹³⁸ an asphalt emulsion is resistant to freezing when no change takes place in 50 ml of emulsion after cooling from 50° to 5° in one hour, reheating and recooling.

(5) Myers' method for testing the demulsibility of emulsified asphalt for road construction is used.¹⁴¹ It consists in stirring and kneading a mixture of 100 g of emulsion and 35 ml of 0.02*N* calcium chloride solution at 25° with a 5/16-inch glass rod. The mixture is drained through a 14-mesh sieve and washed. The beaker, rod and sieve are dried at 163° F and weighed. For quick-setting emulsions, the per cent demulsified should approach 100. For slow-setting (mixed) emulsions, the method is modified by using a more concentrated (0.1*N*) solution of calcium chloride. This method is considered to give more consistent results than the sieving-washing method and the gravel test.

Photomicrographs should be taken to facilitate the production of successive batches of emulsions having the same degree of dispersion. For these tests an emulsion is usually diluted with three volumes of a 2-per cent potash solution. The range of particle size which must be considered in photographing gives rise to difficulties with depth of focus. Haidberg⁸⁶ found means of overcoming these difficulties by using dark-field illumination. The use of a Zeiss epicondenser with a special objective is suggested. Diffraction effects which the smaller particles undergo are eliminated and the size can be measured. The photographic procedure used by Haidberg is successful in obtaining sharp images of all particles, irrespective of depth. In stability tests, determination of the size of small particles is of great importance.

Different methods are employed in studying the characteristics of

bitumen emulsions used for coating road stone. The coating test comprises coating a given quantity of stone with a given quantity of emulsion. Three phases are noted as the materials are mixed together, namely, stiffening time, clustering time, and stripping time. There is no standard stone. Uniform material is used for this test. This test is also a means of differentiating the type of emulsion, *i.e.*, whether quick-breaking, usually clustering and stripping within one or two minutes; intermediate-breaking, clustering and stripping within five minutes, or slow-breaking, clustering and stripping in from 5 to 25 minutes.

The Italian Institute for Road Research applies a test similar to Shimp's test used in concrete practice. A quantity of mineral aggregate is introduced into a cone and saturated with an emulsion. The excess emulsion is drained off, the cone inverted on a table and withdrawn, leaving a cone-shaped body of stone coated with an emulsion. A series of blows is given to the table after certain periods of time. The moment when the cone of material does not collapse or its base broadens is taken to be the moment when the stone is held together by separated bitumen, *i.e.*, when the emulsion is broken. Thus quick-breaking or slow-breaking of an emulsion on limestone may be recognized.²³⁶

Keppeler, Blankenstein and Borchers¹⁰⁹ considered "breakability" an important characteristic of the bitumen emulsion system, which is determined by measuring the amount of bitumen retained by finely broken stone when stirred with the emulsion under standard conditions. Breakability is influenced by such factors as the kind of stone used, the alkali concentration of the emulsion, the concentration of the disperse phase, as well as the softening point of the asphalt.

Weber^{242, 243} described a new test for the breaking of emulsions on stone, which eliminates the effect of evaporation. It is based on the determination of the bitumen separating on the stone under controlled conditions. The process of breaking is interpreted in terms of the amount of emulsifier present and the effect of the stone upon it. Vandone²³⁵ improved the Weber-Bechler²⁴⁴ "breaking index." Geisler and Kleinert⁷⁷ described methods for determining the breaking point of road emulsions.

Caroselli³⁰ proposed a method for determining the breakability of bitumen. This method requires that the emulsion have a bitumen content of 50-52 per cent. Two volumes of alcohol are added to one volume of the emulsion. If the bitumen precipitates as a lumpy mass, the emulsion is classed either as a quick-breaking or a slow-breaking, partly stable emulsion; if the bitumen remains in suspension as finely divided particles, the emulsion is classed as stable. Ten cc of the emulsion is diluted with 25 cc of distilled water in an Erlenmeyer flask. Two cc of 0.02*N* calcium acetate solution is added from a burette; the mixture is shaken one minute, and then heated to boiling. The flask is cooled and the liquid decanted into another flask. The first flask is washed with 5 cc of distilled water and a 0.1 per cent solution of Neptune blue R. G. slowly added from a burette to the liquid until the brown color of the emulsion changes to olive or greenish. If less than 10 cc is required, the

emulsion is quick-breaking; if 10-30 cc is required, it is partly stable; and if more than 30 cc is required, it is stable.⁸⁹

Among the methods for testing asphaltic bitumen is that of separation by adsorption on porous porcelain plates.^{175,185} It has been thought that separation through adsorption is the nearest method to the actual working conditions, because an essential portion of the liquid phase in both cases is removed by filtering. Determination of the other components of the emulsifier in the dried bitumen, as well as the asphaltic bitumen separated on the road, has not as yet met with success. It has been shown by the testing method that the ductility of the separated bitumen is materially lower than that of the original bitumen.

Downing⁵⁷ proposed a modification of the miscibility test for asphalt emulsions. The asphalt emulsion is diluted in the ratio of 50 ml of emulsion to 150 ml of distilled water, whereby results are obtained more rapidly.

A.S.T.M. Tests for Emulsified Asphalts

The American Society for Testing Materials has adopted the following tests for emulsified asphalts [A.S.T.M. Specifications D 397-401/34 T Proc. A.S.T.M., 35, 923 (1935)].

1. Viscosity Test (Saybolt-Furol Viscometer).
2. Distillation Test (A.S.T.M. D 402-36 and I.P.T. Method CB3).
3. Water Determination (Dean and Stark Method).
4. Settling Test. 500 cc of an emulsion is stored in a cylinder for five days and the asphalt content of the top and bottom samples is determined.
5. Sieve Test. The emulsion is passed through a No. 20 U. S. standard-mesh sieve, washed with a 2-per cent sodium oleate solution, and the weight of the material retained on the sieve determined after drying for 2 hours at 105°.
6. Demulsibility Test. The emulsion is treated with a 0.02-per cent calcium chloride solution with continuous stirring at 25° + 0.5°, passed through a No. 14 U. S. standard mesh sieve and washed. The weight of asphalt coagulated is determined and expressed as per cent demulsibility.
7. The miscibility test applicable to the slow-setting type of emulsion consists in adding gradually 50 ml of the emulsion to 150 ml of distilled water and recording appreciable coagulation after standing for 2 hours.
8. Coating Test. The stone is coated with an emulsion, washed, dried, graded, and stored. Data as to whether appreciable coagulation of the asphalt from the water of the emulsion has occurred, and whether the stone is coated uniformly are recorded.
9. The freezing test consists in cooling the emulsion to 0° F for 12 hours after thawing and freezing for three periods of 12 hours each. The emulsion is either homogeneous or broken.

Acidity of the bitumen may be of interest in connection with emulsification. The acidity of a bitumen is expressed as an acid value, or the number of milligrams of potassium hydroxide required to neutralize the free acids in 1 g of bitumen.

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LUBRICANTS AND LUBRICATING OIL EMULSIONS

Introduction

The fact that the principles of adsorption at phase boundaries apply not only to emulsions, but to lubricants indicates a parallelism between emulsification and lubrication.

For certain purposes, lubricating oil emulsions are very desirable, and efforts are being made to make them permanent. Some soluble cutting oils, which are emulsions of water and compounded petroleum oils, are very valuable for lubricating cutting tools. Such emulsions contain a relatively large amount of water and a small amount of oil; thus, they are emulsions of oil-in-water. Some of the soluble cutting oils are not emulsions, but solutions of soaps, or saponified sulfonated fatty oils.⁷ On the other hand, emulsions very often formed in the circulating system of a steam turbine, for example, are very undesirable. They plug oil lines, prevent proper precipitation of impurities, and carry them to the bearings, causing the latter to overheat and to wear. Whenever possible, the occurrence of emulsions in lubricating systems should be prevented. Pure mineral oils are usually used in industry, and their efficiency as lubricants has been found to be improved by the addition of suitable polar materials, such as saponifiable fats and oils. Primarily, the active agent which enables the saponifiable oils to improve the lubricating properties of mineral oils has been considered to be a small percentage of free fatty acid, either pre-existing in the saponifiable oil or formed therefrom by hydrolysis during lubrication. If it were not for the presence of these small proportions of free acids, the saponifiable oils or compounded oils would have a low interfacial tension against water.

Any substance which lowers the interfacial tension causes the liquid to spread over a larger area of the solid. Thus substances lowering interfacial tension should act favorably, as far as lubrication is concerned, because by preventing rupture of the liquid film they keep the metals between which the liquid is placed from coming into direct contact.

This improvement in lubricating oils is covered by a patent issued to Wells and Southcombe,¹⁰⁶ who replaced a relatively large amount of saponifiable oil or fat by a relatively minute amount of a suitable free fatty or other organic acid in order that the amount of acid would be limited and not increase; for if the free acid is present as an impurity or as a hydrolytic product of a saponifiable oil, the amount can increase greatly. Wells and Southcombe¹⁰⁵ called a suitable acid the "germ" which, when dissolved in mineral oils, imparts to them life and activity as a more perfect instrument of lubrication. At the present time, general reports on lubricating oils consider graphite to be the most valuable and important addition agent to lubricants; saponifiable fats and oils or free fatty acids are only a small proportion of the materials used for improving lubrication.

In an investigation of a number of S.A.E.⁴⁰ compounded and non-compounded lubricating oils, including Conoco germ-process oil (typical of the compounded oils) with respect to surface and interfacial tension against water, Roberts^{84a} found no significant difference in either surface or interfacial tensions between Conoco and other non-compounded mineral oils. The values were of the order of 12 dynes/cm for an interface 30 minutes old. The Conoco germ-process oil (compounded with a small percentage of oleic acid) gave a value of 12.5 dynes/cm. This is in agreement with the statements made by Francis and Bennett³⁵ and Harkins,⁴¹ who established the fact that the interfacial tension between water and oleic acid is 15.7 dynes at 20° C. Thus, the addition of oleic acid to mineral lubricating oil can produce no appreciable decrease in the interfacial tension. However, the important factor in lubrication, as mentioned by Francis and Bennett, is chiefly the interfacial tension between oil and metal—a value not susceptible to direct measurements. (Bartell's adhesion-tension method is, perhaps, the most feasible).

Johansen¹⁵⁴ measured the interfacial tension, σ_{pw} of lubricating oils with oleic acid against water, using two samples of lubricating oil, one containing one per cent of oleic acid and having an interfacial tension of 30.1, the other 10 per cent of oleic acid and having an interfacial tension of 14.2. He also studied the difference in the behavior of surface and interfacial tension in an experiment in which the lubricating oil (always containing active substances) was filtered through Floridin (fuller's earth); the active substances were thus thoroughly adsorbed, and the surface and interfacial tension increased because of purification, but the change was found to be greater in the case of interfacial tension (σ_{pw}) than of surface tension (σ_p):

	σ_p	σ_{pw}
Lubricating oil	31.3	29.4
Lubricating oil filtered	31.7	42.6
	0.4	13.2

Thus the interfacial tension of oils was proved to be more sensitive toward foreign substances than surface tension, and orientation was considered to be its reason.

The addition of bituminous matter to mineral lubricating oils, according to Philip,⁷⁹ causes a lowering of the demulsification value. Therefore the constitution of mineral lubricating oils is of importance. Demulsification, in some cases, is brought about by a greater hydrogen ion concentration (higher acidity).

A typical class of Pennsylvania paraffin-base lubricating oils (the so-called Valvoline oils) was investigated by Matbery and Mathews⁶¹ to determine its constitution. They found that it contained a number of saturated hydrocarbons of unknown composition and identified as an isoparaffin mixture (C_nH_{2n+2} , C_nH_{2n} , C_nH_{2n-2} , C_nH_{2n-n} , etc.). The reaction ability increases in this series, but not to such an extent that these hydrocarbons can be identified as olefins.

Fatty oils⁵³ are used alone only for a few lubricating purposes and to some extent mixed with mineral oils. They represent a very small proportion of the total oil used for lubrication. Cup greases which are compounded with saponifiable oils are the most important of the grease lubricants and comprise over half the total production. The saponifiable animal oils include horse and hog fat, tallow, lard and tallow oils, and fish and whale oil. The vegetable oils are palm oil, cottonseed oil, soybean oil, castor oil and rapeseed oil. Lubricating oils⁶ may be compounded with oils, such as linseed, and with fatty oils polymerized with the fluorides of beryllium, aluminum or boron. The polymerization products are subjected to purification (diluted with benzene and purified with 50-per cent alcohol), and added to the lubricating oils. Another example of a synthetic lubricant is that of Chafneux,¹³ who compounded a lubricating oil consisting of 40 per cent of castor oil, 40 per cent of peanut oil, 17.5 per cent of mineral oil, 2 per cent of camphor, 0.25 per cent of acetone and 0.25 per cent of phenyl oxide.

The products⁸³ obtained by the refining of crude shale oil from Scotland include motor gasoline, illuminating, fuel and lubricating oils. Depending upon the nature of the shale, as well as the retorting and refining conditions, the yield of lubricating oils varies. In general, the lubricating oils amount to 6.6 per cent; the proportion of naphtha is 9.9 per cent, burning oil 24.7 per cent, and gas and fuel oil 24.4 per cent. The grades of lubricating oil made by this process are not suitable for steam cylinders, internal combustion engines, or heavy bearings. Hydrocarbon oils obtained from petroleum, coal tar, colophony or mineral lubricating oils lower interfacial tension when incorporated with relatively minute amounts of compounds, such as a 2-per cent commercial "olein" (glyceride of oleic acid), and may be used as a lubricating material.

Petroleum from Baku, Surachan, Balachany, or Bibi-Eibat, when subjected to fractional distillation, is considered a typical Russian lubricating oil.⁹³ These oils have a low cold test. Fractions under 300-400° have a cold test of -80°, while those at 400-500° give -40°. It is known that naphthenic compounds do not oxidize readily; hence those lubricating oils which have a high naphthenic content undergo little change when subjected to oxidizing conditions. The aromatics present can be readily and completely removed. These oils are suitable for use in combustion engines¹⁰³ because they have practically no residue, remain oily, and never adhere to metal surfaces. These lubricants may also serve as transformer and switch oils.

Lubricating Power as a Function of Various Properties of a Lubricating Oil

The physical properties influencing the character of a liquid or a grease to be used as a lubricant are density, viscosity, capillarity (or surface tension), and oiliness. The choice of a lubricant depends also on the conditions of service, namely, whether it is viscous or boundary lubri-

cation, *i.e.*, lubrication of rapidly moving parts (shafts) supplied with an excess of oil under pressure, or lubrication at slow speeds and high bearing pressure, frequently with a very limited supply of oil. In the first case, the frictional values depend primarily on the viscosity of the oil⁸³; in the second case, on the so-called oiliness necessary to maintain a film.

Emulsibility and Viscosity

The lubricating power may be a function of the emulsibility of lubricating oils. In general lubricating practice it is believed that the formation of water-in-oil emulsions is more frequent than of oil-in-water emulsions. The latter are characterized by a lower viscosity than the former; they have a minimum of disperse phase, and it is apparent that no sluggish flow due to emulsification is encountered in practice.

According to Ubbelohde,¹⁰¹ viscosity of an oil used as a lubricant is of great significance in the lubrication of high-speed systems. Whether the viscosity test is a very reliable determination of the lubricating value of an oil has not been ascertained by practical results. Nevertheless, the test is usually carried out according to one of the following three methods: (1) passage of the oil through a standard orifice or capillary; (2) the rise of air bubbles or the fall of metal balls in different oils maintained at the same temperature; and (3) the rate of flow of a drop of oil down an inclined plane (Bailey).

Michell's⁶⁶ ingenious cup and ball viscometer is popular for rapid determination. A metal ball fits into a cup and the thickness of a film of oil interposed is determined by three raised points on the cup, the supply of oil for the film being held by a small groove in the cup, and the temperature of the cup recorded and maintained at that temperature for half an hour.

Absolute viscosities are determined with capillary viscometers, Ostwald's being considered the best. The Vogel-Ossag is a viscometer of the pipette type, but is not generally used. The Saybolt, Engler, and Redwood viscometers are the types commonly known and used.

Albersteim and Ronheim² proposed a viscometer for investigating lubricating oils operating according to the following principle: The oil to be investigated is forced under constant pressure through a narrow channel and the viscosity is determined by the amount of oil flowing through in a given time.

The temperature at which a lubricating oil ceases to flow is of considerable importance, especially for oils used in motor-car engines at various periods of the year, as well as for oils intended for lubrication of refrigerators. Martin⁶⁴ proposed a method for a cold test or a pour point. The oil is poured into a standard (U) tube 1 cm in diameter and is placed in a freezing mixture until it has set; it is then removed, and subjected to a constant air pressure, the temperature at which the oil starts to flow being noted. The solid point plus 5° F is the "pour point." In daily practice, a given low temperature is often specified, and the flow of oil is observed at a temperature corresponding to a definite pressure.

Wilkin, Oak and Barnard¹⁰⁹ measured viscosities at low temperatures under pressure and proved that the laws governing the torque required to crank engines depend on the viscosity of the thin oil film on the walls of the cylinder. Better flow curves are obtained for waxy oils at low temperatures under pressure than for asphalt-base oils; in spite of the lower cold test, the former have an advantage over the latter. Consideration must also be given to the fact that the original viscosity of a lubricant may change on application.

Osborn⁷⁸ noted that raising the temperature of lubricating oils from 60 to 150° F decreases their viscosity from 90 to 97 per cent, depending on their original viscosity, as well as on the nature of the oil. Osborn pointed out that oils having steep slopes in their viscosity-temperature curves are particularly suited for lubrication of machinery where large quantities of water are likely to become mixed with the oil, because of the fact that a relatively small temperature increase considerably decreases the viscosity.

Capillarity

Without doubt, lubrication is a function of the capillary properties of the oils used. Wells and Southcombe¹⁰⁵ assume that a satisfactory lubricant must wet the bearing surface in such a way that pressure causes a thin film of the lubricant to move into the constricted areas. The mechanism of the lubrication process is comparable to the reduction in interfacial tension. Whether the latter is a decided factor in lubrication must be ascertained. It has been proved that vegetable and animal oils, considered good lubricants, have a much lower interfacial tension with respect to water than have mineral oils. A neutral glyceride possesses a similar interfacial tension. In the case of fatty oils, the lowering of interfacial tension is due to the presence of traces of free acid. In lubricating systems, interfacial tension between oil and metal is to be considered.

The interfacial tension of a number of aqueous solutions against mercury have been measured by McLewis,^{80a} Patrick, and others, who found that it was lowered by the addition of all the solutes examined, including mercurous sulfate, salicylic acid, picric acid, neo-fuchsin, morphine, hydrochlorides, caffeine, aniline, and sodium glycocholate. All these substances, except mercurous sulfate, lower the surface tension of water, yet at the same time diminish the interfacial tension against mercury. According to Antonow's law, these substances should lower the surface tension of mercury even more than that of water. Contamination of the mercury surface due to adsorption should be expected. The interfacial tension of mercury has not been found to be raised by the addition of a solute to water, and this agrees with the fact that mercury surfaces are readily contaminated. The interfacial tension between oil and a liquid metal, such as mercury, was claimed to be very much the same as in the case of an oil/water interface. From this it has been deduced that substances lowering the surface tension at the oil/water interface will have

the same effect at the oil/metal (Hg) interface. On the other hand, Harkins' findings^{41,42} indicate that interfacial tension of water against oil lies in the range of 10-45 dynes/cm; water against mercury is 375 dynes/cm; and mercury against oil is of the order of 300-375 dynes/cm. Wells and Southcombe¹⁰⁵ stated that some substances have a low coefficient of static friction when interposed in thin films between metallic surfaces.

Wilson and Barnard,^{110b} measuring the surface tension of various oils, found that substances of low surface tension are not always good lubricants; therefore, this particular characteristic of lubricants, in itself, is not altogether reliable.

Wilson and Barnard,¹¹² state that, even granting that the results against mercury surfaces roughly parallel those against other metals, it must be emphasized that these results do not have any direct bearing on the coefficient of friction between partially lubricated surfaces, in spite of frequent assumption to the contrary. Lowering of the interfacial energy is only a measure of the tendency of some constituent to concentrate at the metal surface; whether or not this results in lowering the friction coefficient depends almost wholly on the nature and structure of this adsorbed film. Static friction measurements, in which the effect of 2-per cent additions of *p*-cresol and stearic acid to mineral oil are compared, show that both lower the surface tension against mercury; both are, therefore, concentrated at the metal surface. However, although the stearic acid film greatly lowers the coefficient, the *p*-cresol film appears to give even slightly higher coefficients than the plain oil. It is believed by Wilson and Barnard that a partial lubricating film, to be effective in reducing friction coefficients between metal surfaces under high pressures, must have the properties of a solid rather than of a fluid film, and must be of colloidal rather than of ordinary molecular dimensions. *p*-Cresol apparently fails in one or both of these specifications, but stearic acid possesses them to a high degree. Bhatnagar and Garner^{6a} gave results with different fatty acids dissolved in mineral oil; linoleic acid seems to be more highly adsorbed than palmitic and stearic acids. It does seem conceivable, however, that the lowering of interfacial energy between oil and metal surfaces could be determined approximately by measurement between oil and mercury, the only pure metal which is liquid at ordinary temperature.

Wells and Southcombe¹⁰⁵ considered that the permanence of films is dependent on diminished interfacial tension between the oil and the metal in contact with it. They further state that if such a film were broken, the possibility of its reuniting to form a continuous film depends entirely on a reduction in the interfacial tension. Holde and Singalowsky⁴⁸ considered surface tension measurements significant for lubricants. Ubbelohde¹⁰¹ indicated the importance of surface tension, as well as the angle of contact, for the penetration of an oil into the narrow spaces existing between the bearing and the axle. An attempt has been made¹⁰¹ to prove that if the evaporation of water could be prevented from such substances

as cellulose, alkali and molasses solutions, they too would serve well as cheap lubricants. But all these substances have a high surface tension and a large angle of contact in comparison with mineral lubricants and fatty oils.

Assuming that a lubricant must penetrate the narrow spaces between journal and bearings, a liquid which does not wet the solid surface cannot be considered a lubricant. Eitner²⁸ patented the addition of petroleum pitch to increase the wettability and to decrease the interfacial tension. Dallwitz-Wegner¹⁸ found that lubricating power depends on the force with which the oil is adsorbed by the metal, and the tenacity of the oil film on the capillarity of the oil and the metal of the bearing and journal. A series of methods for the determination of these properties was proposed by Dallwitz-Wegner, who found that the lubricating power of an oil increases with decrease in its angle of contact and its surface tension.

Adsorption and Wetting Ability

According to recent theories of adsorption,⁵⁷ the surface of an adsorbent is considered to be a field of force, which is the resultant of the residual valences of the atoms on the surface. Adsorption consists in saturating these valences with secondary valences of the adsorbed molecules. The heat of adsorption of a liquid on a solid is called the "heat of wetting."

Bachmann and Brieger⁶ state that the physico-chemical force of attraction is the force by which the oil or a constituent of the oil is selectively adsorbed by the metallic surface, and this finds direct expression in the heat of wetting. In a table compiled by these investigators on the heat of wetting of various powders by different liquids, no values higher than 80 cal. per gram of adsorbing substance were obtained. The small heat effect prevents its determination at the solid metal surface; therefore a much larger surface in a granular form must be exposed to the liquid. The following table shows the relation of heat of wetting to the lubricating ability:

Oil	Heat of Wetting (Calories)	
	Temperature increase (°C) per 20 g of copper diluted with benzene	Temperature increase (°C) per 100 g of copper without benzene
Castor oil	0.018	11.75
Linseed oil	0.019	14.45
Machine oil distillate	0.023	14.55
Refined machine oil	0.010	6.65
Paraffin oil	0.006	3.85
Petroleum	0.007	5.3
Benzene	0.003	22.0
Petroleum+1% oleic acid	0.029	20.5

When the temperature increase is plotted against time, the curves obtained show a marked change in slope due to evolution of heat by the wetting of the copper by the oil. The distance between the prolongations of the first and last portions of the curve is taken as a measure of the heat of wetting. Benzene appears to have a very small heat of wetting;

therefore the amount adsorbed by the metal will be small. According to Dallwitz-Wegner,¹⁸ the force of friction producing strain on a lubricated bearing is dependent on viscosity and heat of wetting, as well as on the design of the bearing.

$$F = \phi \cdot \frac{\eta}{\epsilon \beta}$$

where η = viscosity; β = heat of wetting; ϕ = constant, depending on the radius of the bearing, the relative speed of the lubricated parts, load, etc., and ϵ = the shortest distance between surfaces.

Naturally, higher wetting heats are to be expected between graphite and an oil than between a metal and the same oil. According to observations made by Acheson (G. P. 230,586), graphite is an oleophilic substance. Colloidal graphite dispersed in an aqueous solution is replaced immediately by oil from the water phase and adsorbed by it. This is a typical case of adsorption displacement, for the water molecules present in the graphite are displaced by oil molecules. Therefore, it is to be expected that the wetting ability of oils in relation to graphite is especially high, and this would explain why graphite is such an excellent "oil saving" agent, for it permits the formation of a very thin, stable and viscid oil film, such as would be expected from a good lubricating oil.

The heat of wetting, which was neglected in earlier investigations of mineral-oil lubricants, has been determined from the angle of contact by Duffing,²⁵ who found that it depended not only on the oil, but also on the surface which it touched. In general, the angle of contact is smaller and the wetting ability better the greater the pressure. In the case of alloys such as bronze, the surface relationship is more complex.

According to Duffing,²⁵ the "contact angle" which a lubricating oil forms when placed free against a lubricated metal determines its lubricating power. An oil that has a high wetting pressure against a lubricated metal is a better lubricant than that with a smaller wetting pressure; for the greater the wetting pressure, the greater the lubricating friction. Under these conditions the contact angle serves as a reagent, its value determining the degree of lubrication. In testing a series of cylinder oils (A, B, C) with contact angles of 20°, 25°, and 40° respectively, the corresponding lubricating power was 1:2:8, or inverse as the third degree of the contact angles of the respective lubricants.

Foreign particles in an oil enlarge the contact angle and decrease the wetting pressure. An increase in the surface tension is also undesirable. Tar oils, for example, possess a relatively high surface tension and, although they have a relatively small contact angle, are not good lubricants. Therefore, in order to increase the sphere of action of their molecules, the cohesion pressure must be increased. By molecular attraction in the lubricating layer a wetting pressure K_b is produced from the cohesion pressure of the lubricant and, in general, the cosine of the contact angle indicates what portion of the cohesion pressure K has been converted into the molecular wetting pressure K_b , because

$K_b : K = \cos \theta$ when θ is the contact angle. Thus $\cos \theta$ is the degree of action of a lubricating oil. The lubricating power of the lubricant and also the lubricating friction depend on the wetting pressure K_b (which is several hundreds). The lubricated metal also plays its part, depending upon the contact angle, and this determines its suitability for a particular lubricating oil.¹⁸

Oiliness

Two oils, although similar in their chemical and physical properties, may still vary in the amount required to produce minimum lubrication. Therefore Duffing and Dallwitz-Wegner defined the lubricating ability of such oils as the inverse of the amount of oil required to effect the minimum in lubrication. The tendency of oils to form an adsorbed layer in the interface varies for different lubricants. It is considered to be a function of the "oiliness" of an oil. Wilson and Barnard¹¹¹ called "oiliness" the property of lubricants by virtue of which one oil has a lower coefficient of friction (generally at low speeds and high loads) than another of the same viscosity. In stopping and starting a machine, the speed is sufficient to maintain an oil film in the bearings (viscous lubrication). By using a lubricant of high oiliness, the maintenance of an oil film is assured even when the bearing is at a standstill (boundary lubrication). In the case of boundary lubrication, the adsorbed film is a plastic solid rather than a fluid, having the effect of smoothing surface irregularities and minimizing metal-to-metal contact. The structure and physical characteristics of this film have great significance in determining its efficiency in lowering friction. Hardy³⁹ and his co-workers, in their researches on ruptured films and boundary lubrication, assumed that this type of friction follows Amonton's law of sliding friction, a friction which is proportional to the weight of the slider and independent of the area of contact.

Wilson and Barnard¹¹¹ pictured a film of lubricant several molecules thick, built up according to the orientation of molecules described by Langmuir.⁵⁷ Langmuir considers oiliness to be dependent on the chemical forces called into play between the active part of the oil molecule and the solid surfaces of the bearing. Much evidence has been found to bear on the fact that oiliness is a function of the chemical constitution of the lubricant.

Active substances are instrumental in causing oiliness. Rayleigh,⁸¹ Woog,¹¹³ Trillat,¹⁰⁰ and Langmuir,⁵⁷ studying the subject of oiliness, found that active substances present in the oil form oriented layers on the solid surfaces; the hydrophilic group is thus turned toward the solid surface and the hydrophobic methyl group away from it. In lubrication, smooth surfaces of methyl groups glide over one another because of their small mutual affinity. Langmuir has shown that the lubricating film may be worn off rapidly when exposed to wear. This occurs much faster with a monomolecular than with a polymolecular film. In addition to the thickness of a lubricating film, factors favoring the rebuilding of the film

when worn off must be considered. Therefore the presence of an oil with saturated molecules is preferred, since it spreads readily and may transport active molecules dissolved and redissolved in it into the space to be lubricated.^{35a}

Various Tests for Lubricating Oils

Oiliness

There are various methods for measuring oiliness in connection with the mechanism of lubrication. Hardy³⁸ placed a slider on a lubricated surface and calculated the coefficient of static friction from the minimum weight required to cause the slider to move. Koethen⁵⁵ improved Hardy's method by equipping his slider with three steel bearing balls tightly clamped together. Only a small surface comes into contact with the lubricated surface, but by a slight rotation of the balls fresh surfaces can be exposed. The slider was placed on a lubricated surface and inclined at an angle to the horizontal, the minimum angle necessary to move the slider being noted.

The Deeley machine measures the coefficient of friction between plane surfaces at low speeds. Hardy and Doubleday⁴⁰ and Wilson and Barnard¹¹² used a modified method for determining coefficients of static friction between lubricated metal surfaces. Wilharm¹⁰⁸ combined the methods of Hardy and Doubleday and Wilson and Barnard in the construction of an apparatus consisting of a slider on a special inclined plane, and detected the instant of slip by making an electric contact.

Wilson and Barnard¹¹¹ reported other measurements in connection with oiliness, *i.e.*, the interfacial energy between oil and mercury, the electrical resistance, the rate of formation of an adsorbed film on a metal surface, and the clogging of fine metal capillaries through which a lubricant is forced. Results obtained by these methods show that the static friction test is the best for determining oiliness, but that it should be supplemented by measurements of the thickness of the adsorbed films at high pressures in order to clarify the mechanism of action of different constituents in lubricating oils. For instance, animal and vegetable oils invariably are more oily than mineral oils. The blending of large amounts of neutral glycerides with mineral oils greatly improves their oiliness, but the same results are also obtained by adding small amounts of fatty acids or oil-soluble soaps. The fatty acids which occur in commercial oils are never pure chemical entities, but rather mixtures of a considerable number of fatty acids in varying proportions.

When the less stable ingredients of lubricating oils are oxidized, lower as well as higher fatty acids are formed. The latter are more readily subject to further changes than the former. Redgrove⁸² investigated the effect of fatty acids on the lubricating properties of an oil by measuring the coefficient of static friction of a mineral lubricant to which was added one per cent of castor oil and oleic, crotonic, palmitic, valeric and butyric acids. In agreement with the results obtained by Hardy, it was found

that the lower fatty acids, under conditions of lubrication, did not decrease the coefficient of static friction of mineral lubricants. It appears that the presence of polar groups in short-chain or low molecular weight acids does not contribute materially to their lubricating value.

The lower members of the normal fatty acid series up to capric acid are liquids at ordinary temperature; the higher members in the series are waxy solids which boil without decomposition only under reduced pressure.

Polarity and Adhesion of the Lubricant

It is recognized that friction between polished surfaces is caused by unbalanced forces of molecular attraction acting across the interface, and the lubricant is placed there either to neutralize completely the unbalanced forces (perfect boundary lubrication) or to separate the rubbing surfaces beyond their effective fields of force (viscous lubrication).

To neutralize forces acting at metal surfaces, physicochemically active molecules are required. Polar molecules exhibiting secondary or residual valence are known not only to be attracted by forces of the metal surface but to orient themselves with respect to the surface. The orienting character of polar molecules is known from the works by Marcelin,⁶² Devaux,²² Langmuir,⁵⁷ Adam,¹ and Woog.¹¹³ Furthermore, it has been realized that the strength of attraction between the lubricant and the metal surfaces depends not only on the polarity of the lubricant, but also on the physical and chemical nature of the metal surface. The specific forces of attraction emanating from the metal surface and the polarity of the lubricants should be considered when improvement of lubrication is planned. It has been established by Clark and co-workers^{15,16} that forces of attraction between metal surfaces are neutralized by strongly polar molecules, such as chlorinated esters of long-chain fatty acids and short-chain monohydric alcohols. The fields of force emanating from metal surfaces are neutralized by forming an oriented film and by regimenting hydrocarbon molecules in the liquid body of the lubricant. Clark's x-ray investigations indicate that the type and thickness of the film depend on the polar compound used as well as on the metal. Strongly polar molecules of certain chlorinated esters were found to form films of unusual thickness (of the order 9000 Å) and regularity of arrangement. Polar compounds tested on iron, zinc, cadmium, and copper were: stearic acid, methyl stearate, octadecylchlorostearate, ethyldichlorostearate, monochlorodiphenylene oxide, trichlorophenol, trichloronaphthalene, and methyldichlorostearate.

The theory of viscous lubrication is rather well developed, but not that of boundary lubrication. Both viscous and boundary lubrication are obtained by the presence of a definite minimum amount of oil upon which the reduction of friction depends. The adhesion of an oil is of importance in boundary lubrication. Langmuir considered that the forces acting (primary and secondary valences) are physico-chemical in nature, and that the polar groups, which determine the symmetrical structure of

the molecule, originate these forces. Harkins is of the opinion that the strongest polar groups are directed toward the adsorbent only when it is more polar than the substance adsorbed, and when the forces acting increase with increase in molecular weight. Dunstan and Thole²⁷ assume that the lubricant molecules enter into physico-chemical combination with the metal surface. Haure⁴⁵ states that a viscous oil, which shows only a slight adhesion, is a poor lubricant, whereas a slightly viscous oil with good adhesion properties is an excellent lubricant.

Compressibility and Tensile Strength

Two other physical properties influence the character of a liquid lubricant, namely, compressibility and tensile strength, but very little work has been done on either of them. Doubts have been expressed in regard to the significance of compressibility and tensile strength as determining factors in the classification of oils to be used as lubricants.

The compressibility of liquids is very small. Methods for measuring it are based on the works of Canton,^{11a} Oersted,⁷⁵ Jamin, Amaury and Descamps,^{52a} Guglielmos,^{36a} DeMetz,^{65a} Richards and Stall,^{83a} Bridgman,^{8a} Seitz and Lechner,^{85a} and others, and the instrument used is the piezometer. Compressibility may be defined as the contraction of a liquid in a unit volume per atmosphere. If the pressure is p and p' and the corresponding volume V and V' , then compressibility, C , may be computed according to the following equation:

$$C = \frac{1}{V} \frac{V - V'}{p' - p}$$

To convert into megadynes, the value obtained is divided by 1.0137; multiplying by 10^6 increases it.

By experiment, it was found that mercury has the smallest value of compressibility; the compressibility of aqueous solutions of salts is smaller than that of water, and the smaller the value the more concentrated the solution. According to Skinner's investigation,^{87a} the decrease in compressibility with concentration is large for electrolytes and small for non-electrolytes. Barus^{5a} measured the compressibility of such colloids as gelatin and albumen in water, as well as of rubber and ether, and found that the compressibility of the solute is almost equal to that of the solvent.

The apparatus for determining tensile strength may be a machine of the pendulum type (Henry L. Scott & Co.) in which the pointer remains in position when the specimen breaks and is reset by means of a handle suspended from a curved quadrant. The Mullen tester (B. F. Perkins & Sons, Inc.) consists of a flexible circular diaphragm 6.44 sq cm in area and a pressure chamber filled with glycerin. The test specimen is held over the diaphragm by a clamp with a round hole one sq in in area; when pressure is applied under the diaphragm the material is forced into the hole and "bursts" the sample tested. This pressure is read from

a dial graduated in 0.5-lb divisions and is increased at a rate of 2 lbs per second at a temperature of 77° F. Ten tests are averaged.

The lubricating capacity of an oil may be measured by the potential difference existing between the lubricated and the unlubricated portions of a metal, as suggested and demonstrated by Evans.²⁹ Similar observations were made by Hackford³⁷ in practical tests on Diesel engines.

Resistance to Emulsification and Sludge Formation

One of the most important requirements of mineral or crude oil products used as lubricants is that they shall not form emulsions with water, for oils in general possess emulsification properties. As a matter of fact, some oils emulsify, and others do not, under the same conditions, *e.g.*, leakage of water into an oil system, churning of an oil with water by rapidly moving surfaces, etc., particularly a steam turbine equipped with a pressure lubricating system. Sometimes emulsions are produced by very rapid circulation, which can be eliminated by increasing the settling capacity of the system, decreasing the rate of agitation, and giving more time for separation from the water. An increase in the capacity of the system does not decrease the velocity of the oil circulation except in the pump. The velocity with which the oil is circulated is determined by the speed and capacity of the pump. The value of an oil as a lubricant is dependent largely on the joint properties of the oil and the bearing metal and to a lesser extent on its ability (1) to resist emulsification and (2) to separate readily should an emulsion form. In other words, an emulsified oil (cutting oil) may be a good lubricant, but the film which reduces friction cannot be maintained with an oil-water mixture. Of course, very often the water present in such emulsions contains salt in solution, and the electrolytes forced through the bearings may corrode the journals of the steel shaft.

The steam turbine favors the formation of emulsions. This indicates, therefore, that oil for turbines must be of such a nature that it separates readily from water. The kind of water, the boiler steam pressure, the speed and temperature of the journals, as well as the character of the oil are determining factors in emulsification. If the mixture formed is permitted to remain in a state of rest at a temperature which reduces the viscosity of the oil, after an interval of time the water may settle out and separate completely from the oil.

The presence of water in transformer and switch oils is a very disturbing factor, because their insulating ability decreases with an increase in water content. Motor oils, when emulsified, are not so efficient in keeping an engine cool. This is due to lack of efficient lubrication, causing greater friction and generation of excess heat in the bearing rather than to any deficiency in heat adsorption by the oil.

Damany¹⁹ determines the emulsified water in lubricating oils by pumping the oil through a cylindrical container the walls of which serve as a condenser. The change in the capacity of the inside condensers is measured with a Trioden lamp and a rotation circle.

Allen and Jacobs,³ in a bulletin issued by the U. S. Bureau of Mines, state that water in a lubricating oil forms emulsions which tend to lower the durability of the oil and makes it less efficient as a lubricant.

Emulsification and sludge formation are two principal causes of difficulties encountered in lubricated machinery, for the stability of an oil can be determined only under actual working conditions. Oil deterioration has been ascribed to many causes, principally oxidation, with polymerization and condensation next in order. Snyder⁸⁹ proved that no changes occur when oils are heated in sealed tubes up to 250° for five months with and without copper; but, when oxygen and inert gases, such as nitrogen and carbon dioxide, are used, sludge is formed only in the presence of oxygen. Haslam and Trobich⁴⁴ found a similar effect, but, in addition, after deterioration of the oil had begun, condensation and polymerization products were formed. It is not an established fact, but there are certain indications that deterioration is proportional to the percentage of unsaturated compounds present in the oil. Ford,³⁴ studying this problem, found that the quantity of sludge formed is proportional to the amount of unsaturated hydrocarbons contained in the oil, and that a direct relationship exists between the state of unsaturation of the original oil and its stability.

Stability

Certain tests to determine the stability of an oil by measuring its degree of unsaturation are recommended for practical application: (1) iodine value; (2) the Formolite test of Nastjukoff⁷¹; and (3) Nuttal's test for surface tension. A pure, saturated hydrocarbon oil is considered as having little or no affinity for water or aqueous solutions of various substances; but an unsaturated hydrocarbon oil possesses a marked affinity for water, caused by the residual valence of the double bond, and hence gives lower interfacial tension values.

Stability may also be determined by tests in which the oil is subjected to heat and oxidation for a definite period of time and then examined: (1) The Michic sludge test; (2) the Kissling test for coke-forming values; and (3) the Steager test for sludge acidity and the presence of superoxides (superoxides are determined by a decrease in the tensile strength of cotton when immersed in oil and heated in a copper container for 300 hours at 112°).

Sligh⁸⁸ heated 10 g of oil in special flasks at 200° for 2½ hours in the presence of oxygen; Mead⁶⁵ investigated temperature influence; Muszatti and Volterre⁷⁰ considered 200° to be the most suitable temperature; Snyder⁸⁹ and Steager⁹² as well as Baader⁴ studied the catalytic action of metals upon oils; Hotlyn⁴⁹ heated small amounts of oil in porcelain dishes at 250° under atmospheric pressure and examined the oil microscopically to ascertain whether it had become heterogeneous and whether sludge was settling out.

It was recommended that tests for determining stability be conducted at comparatively low temperatures. To determine the extent of

deterioration of an oil, measuring its rate of deterioration was suggested, although this is not general because many reactions which proceed to completion are slow.

The durability of lubricating oils may be determined by the oxidation test.³⁰ Testing oils by the oxidation process is founded on the fact that the oil, very finely divided, permits measuring the rate at which oxygen is taken up. The dispersion is obtained by means of a special catalyzer, while the rate of absorption is measured in a special apparatus, the oxidizer. Prerequisites for the measurement are a certain catalyzer and a fixed temperature (100°). For each oil a typical line with a definite inclination is obtained. For different kinds of oils, the following values were obtained.

White oils	0.030
Insulating oils	0.060
Turbine oils	0.080
Motor oils	0.100

From these values curves are derived from which the average life of a given oil can be calculated. By means of the oxidizer the degree of aging of oils in use may be determined. By aging oils with definitely known quantities of oxygen, the abnormal aging of oils in practice is easily recognized.

All lubricating oils should be tested for acidity, moisture, hard and soft asphalt, fatty acids, sulfur, carbon residue, wax-like substances, naphthenic acids, sulfonated oils and soaps and resins; some of these substances are oxidation products of mineral oils. Traces of the latter products were found by Bryan¹⁰ in every compounded lubricating oil.

Asphaltic resins, soluble in oil and petroleum spirit, are responsible for the discoloration and increase in the viscosity of an oil, and can be removed by charcoal and fuller's earth. Asphaltenes, insoluble in petroleum spirit, but soluble in benzene, are formed by the oxidation of resins.

Testing for coke is also important because of the tendency of an oil to deposit carbon when burned. For instance, in the internal combustion engine of a motor car, carbon deposited on the cylinder head acts as an insulator and causes the entering fuel to become overheated, so that knocking occurs.

Dimmig,²³ believing that surface tension at the water interface is a criterion of the value of an oil, used a special pipette for the determination of surface tension and found for each oil a constant, K :

$$K = \frac{\text{cc per 100 drops in } 0.01N \text{ NaOH}}{\text{cc per 100 drops in distilled water}}$$

the higher the value of K , the better the oil.

Emulsification and Demulsification

Suitability of an oil as a lubricant cannot be properly said to depend on its emulsification or demulsification characteristics. The two pro-

perties are to a certain extent, at least, parallel, in that adsorption on metal, which is essential in boundary and viscous lubrication, requires the presence of polar groups in the oil, and essentially similar polar groups are necessary for the formation of water-in-oil emulsions.¹⁵ It is not denied that ease of emulsification is detrimental in internal combustion engines; but on the other hand, oils which will not emulsify cannot be satisfactory lubricants, because, in removing the components responsible for emulsification, the ability of the oil to adsorb on metals is necessarily decreased. Adsorption at a water interface and on metal are essentially analogous and parallel phenomena and require similar properties.

The "demulsibility" of an oil is determined from the number of cc of clear oil above the emulsified layer, less the amount of water contained in the oil. In practice, demulsification tests are divided into (1) those in which the oil is mechanically agitated with water, and (2) those in which the water and agitation are provided, at least in part, by blowing steam into the oil. The steam test more nearly reproduces turbine conditions, and steaming provides a good degree of agitation.

To determine the emulsification values of lubricating oils used in steam engines, steam turbines and crank cases, Conradson¹⁷ proposed this test method: 20 cc of distilled water and 100 cc of oil are poured into a suitable container; the mixture is churned by steam passing through it at ordinary pressure; the container and mixture are immersed in a water bath at 130° F for one hour, after which they are removed and the following determinations made: (1) the volume of separated clear or turbid water; (2) the volume of separated clear or turbid oil from which the percentage of demulsification is determined; (3) the volume of separated emulsified layer (indicates the ability of an oil to form an emulsion); and (4) the percentage of water or moisture in the separated oil (deducted from the "demulsification value").

Philip⁷⁹ proposed a method whereby the ability of an oil to resist emulsification is measured directly. His apparatus consists of an electrically-driven stirrer operating at 350-400 r.p.m.; 500 cc of an oil is mixed with 500 cc of water at 100° and stirred until a homogeneous mixture results, after which it is poured into a graduate and left standing until layers form. After 24 hours, the volume of oil is read and the percentage calculated from the amount of oil originally tested. Philip calls this percentage the "demulsification value" of an oil. According to Philip, mineral lubricating oils having a demulsification value of 90 per cent or more give no trouble due to formation of emulsions when used in force-feed or pressure lubricating systems.

The demulsibility test adopted by the Technical Committee on Lubricants and Liquid Fuels of the Federal Specifications Board is as follows: 27 cc of the oil and 53 cc of distilled water are poured into a 100-cc graduate of 1 inch inside diameter, heated on a water bath to 130° F and stirred with a rotating paddle at 1500 r.p.m. for five minutes, after which treatment an emulsion forms. Readings of the line of demarca-

tion between the layer of oil and the emulsion layer are taken every minute. The rate of separation of the oil increases up to a certain maximum and then decreases; the maximum value in cc per hour, called "demulsibility," is recorded as the numerical result of the test. This test is used for motor oils and similar classes of lubricants. The Federal Specifications Board¹¹ requires a demulsibility of 300 for steam-turbine oils, as well as for most other oils to which the test is applied. For example, if the demulsibility is 400 and the oil has not settled out in 3 minutes, it has failed to meet the requirements. But, on the other hand, even an ideal oil cannot give an emulsibility value greater than 98 per cent, because 2 per cent is drainage loss. Obviously, other liquids than distilled water can be used with success in demulsibility tests. The Prime Movers Committee of the National Electric Light Association⁷² suggested a solution containing 3 per cent of sodium chloride and 1 per cent of sodium hydroxide.

An almost colorless oil which has been filtered many times does not as a rule emulsify as readily as one that is highly colored. There is no uniformity in the influence exerted by various impurities on demulsification.

Langston⁵⁹ reports that elimination of waxes from oils by more complete refining decidedly increases their demulsibility, while Philip⁷⁹ claims that the addition of paraffin wax to mineral lubricating oils in general does not decrease their demulsification value.

The fact that small admixtures of fatty oils sometimes do and sometimes do not alter the demulsibility of lubricating oils is considered to be due to residual free fatty acids and/or rancidity in neutral fatty oils, and/or whether they contain or are composed of free fatty acids. The presence of acids such as naphthenic acids or those left in oils by improper refining (sulfuric or sulfonic acids), or acids formed in lubricating oils by oxidation under high temperature and pressure conditions, which may exist at the bearing surfaces, may cause a rapid decrease in demulsibility.

Methods for the Preparation of Lubricants and Lubricating Oil Emulsions

Sutherland⁹⁷ stated that emulsification in lubricants might be caused by sulfur compounds present in the oil used as the result of sulfuric acid treatment. Terry and Craig⁹⁸ emulsified lubricating oils in sulfuric acid at 55-65°, added water, and removed the soluble sulfonic acids. Southard⁹⁰ patented lubricants made up of a highly viscous mineral oil to which 5 to 20 per cent of aluminum stearate was added. Zelikow¹¹⁶ compounded a lubricating grease by heating mazout having a viscosity of 4° Engler at 50° and mixing it with commercial Vaseline and a naphthenic soap "Solidol T"; paraffin mazout may be used likewise. Rosetuikow⁸⁵ molded lubricants using briquettes made of acid mineral tar neutralized with lime at 100°; fresh or used florida earth was used

as an adsorbent. Universal Oil Products Co.¹⁰² obtained lubricants by steam distillation of oils in an expansion chamber, condensing with aluminum chloride, and refining with steam or distilling in a vacuum.

I. G. Farbenindustrie A.-G.³² prepared lubricants by cracking and dehydrating paraffin oils, polymerizing and condensing the product obtained in the presence of a catalyst and then separating into substances rich and poor in hydrogen.

Imperial Chemical Industries, Ltd.⁵¹ patented a polymerization process for the preparation of lubricating oils. I. G. Farbenindustrie A.-G.³¹ cracked lubricants of low viscosity and high hydrogen content, obtaining oils such as crude benzene and "anthracene oil," which are polymerized and condensed in the presence of cyclic hydrocarbons, *i.e.*, naphthalene- and tar fractions. Decavel and Roegiers²⁰ describe an electric discharge method, "Elektrion Process" by which mineral oils are treated with hydrogen at low pressures. Through the electro-ionization of oils, they acquire high velocities and low temperature coefficients of viscosity. Oils obtained in this manner have increased lubricating value, and are especially useful in boundary lubrication.

The Ölwerke Stern Sonneborn⁷⁶ prepared lubricating emulsions by mixing limewater with a distillation product of lignite tar. Tar distillates may be completely or partially replaced by oil or oil mixtures. Certain viscous emulsifiers which will withstand a temperature of 50° may be added to produce a stable emulsion.

Whitcomb¹⁰⁷ improved the stability and quality of lubricating-oil emulsions by adding an alcoholic soap solution, thereby reducing the surface tension to a minimum. He found that amyl alcohol or fusel oil gave the most promising results when used in the following proportions: 1 lb of potassium carbonate-fish oil soap, containing about 65 per cent of water; 4 oz of commercial amyl alcohol; 1 gal of lubricating oil (specific gravity 88-90), and $\frac{1}{2}$ gal of water. The amyl alcohol is stirred carefully into the soap solution and the lubricating oil added slowly with stirring until the mixture assumes the appearance and consistency of an oily salve; after this, water is added, producing a creamy emulsion.

Kurata⁵⁶ produced a lubricating compound consisting of 60 parts of a mineral oil and a water solution of a plant albumin, such as soybean, 40 parts of a mineral preservative, such as middle oil, *i.e.*, 2 parts of coal-tar distillation product (naphthalene, carbolic acid, or creosote) and 4 parts of alkali (sodium carbonate or calcium oxide), the latter preventing the lubricant from corroding the metal, and 150 parts of water. Heitmann⁴⁶ obtained lubricants by leading vapors or gases, such as compressed air, under pressure into a container partially charged with a lubricating oil and adding water from the top; a stable emulsion is formed. Farbwerke vorm Meister Lucius Brüning³³ patented an emulsifier for lubricants containing humic acid from black humus (Kasseler's brown fossils, which oxidize and are converted into a dark-colored, high molecular, aromatic carboxy-acid, soluble in alkali). Certain plant formations (causto-bioliths), especially humic acid from coal, are valuable

emulsifiers after oxidation with nitric acid or with air and nitric acid. The oxidation products are dissolved in alkalies, such as ammonia, sodium carbonate, sodium tetraborate, or sodium acetate, in the ratio of 3 to 5, stirred for a short time with the lubricating oil, and then diluted without destroying the permanence of the emulsion formed. This type of emulsion, when dried, may be redispersed by addition of water. When 80 parts of a 20-per cent mixture of a sodium salt and brown coal are oxidized with air and nitric acid and stirred with 20 parts of a lubricating oil, a homogeneous, highly viscous liquid is obtained.

A satisfactory lubricant, in many instances superior to ordinary cylinder oil, is obtained by emulsifying cylinder oil. For this purpose saturated or superheated steam made of 50 per cent water and 50 per cent cylinder oil are emulsified, using 0.015 to 0.02 per cent of calcium oxide.⁸⁰

"Hydro-formed" mineral oil (preferably highly naphthenic), *e.g.*, a lubricating oil obtained by destructive hydrogenation at 460-540° under 250 atmospheres and a suitable contact time, is emulsified by using oil-soluble sulfonates, ethanolamines, or ethylene glycols as emulsifiers.⁵² A sticky, emulsified grease may be prepared from a lubricating oil. A calcium soap is incorporated into a lubricating oil, the mixture cooled, and a dispersion of rubber in oil added. The amounts taken are 5-15 per cent of lime soap, less than 5 per cent of uncoagulated latex, and less than 5 per cent of water.⁶⁹

Hughes⁵⁰ patented a process for making a cutting oil exclusively from mineral oil and having such properties that, when mixed with water, it forms an emulsion. The mineral oil used was derived from relatively heavy Texas crude petroleum distillate. Dunham²⁰ produced a liquid paraffin from lubricating oils by treating with sulfuric acid in an amount depending on their state of purification. After stirring is completed, the sludge is removed, the sulfonic acids are neutralized with a solution of ammonia and alcohol, and the liquid filtered through a decolorizing agent, such as fuller's earth.

A lubricant may be prepared from a mineral or vegetable oil, an emulsifying agent and water in which methyl stearate (2-10 per cent by weight of the oil) is incorporated.⁹

Oil emulsions for use as lubricants, or as cooling liquid for combustion engines, consist of one part of a suitable oil, $\frac{1}{4}$ - $\frac{1}{2}$ part of sodium nitrite, and 100 parts of water. In the case of cast iron, the emulsion should contain 0.2 per cent of the nitrite and for wrought iron, 0.025 per cent of the nitrite should be present in the emulsion.⁴³

Water-in-oil emulsions containing less than 90 per cent of water with 1.8 per cent of potassium soap and 3.2 per cent of candelilla wax, or 1.4 per cent of potassium soap, 1.6 per cent of candelilla wax and 2.5 per cent of tallow have been claimed as extreme-pressure lubricating emulsions. The free alkali content is low; the pH must be much below 12. Glycerin may be added as an antifreeze agent.^{110a}

Herrmann and Rochner⁴⁷ prepared an emulsifiable lubricating oil for metal treatment, such as cutting, drilling, etc. A sulfur-containing agent

was added to the hydrocarbon lubricant and an alkali, such as the resin or alkali soaps of a sulfonated mineral oil, was used as emulsifier. For example, crude maize oil (70 per cent) and a fat (20 per cent) are heated with flowers of sulfur (10 per cent). Sulfur may be introduced also directly in the lubricant. If hard water is used in the preparation of the emulsion, adding a strong alkali soap to the lubricating oil is recommended.

de Cew¹² claimed an increase in the lubricating value of emulsions used on cutting tools by applying colloidal lubricants or fine solid particles. Owing to the high pressure and the high temperature at the point of contact and at the cutting edge, the lubricating value of the oil globules is not as great as it might be, because the viscosity of the oil is greatly reduced by the high temperature when it comes into contact with the metal and the edge of the tool. The decreased lubricating value increases the friction existing at the surface. By mixing oil with graphite its lubricating properties can be improved; Acheson was the pioneer in the use of graphited lubricants. Steinitz⁹⁴ stated also that the lubricating action of a mineral oil increases when colloidal graphite (2 per cent Kollag) is added. Walger¹⁰⁴ likewise is of the opinion that colloidal graphite markedly decreases the friction coefficient of a lubricant in a state intermediate between viscous and boundary lubrication, which involves not only its viscosity, but other properties as well. Graphited lubricants consisting of an emulsion composed of 20 parts by weight of degas freed from fatty acids, 16 parts of kerosene, 75 parts of water, 8.7 parts of turpentine and 4.4 parts by weight of aqueous ammonia, with 30 parts of graphite suspended in the emulsion were patented by Thorpe.⁹⁹ Kerosene may be used as a diluent for the lubricant.

Suspensions of graphite in water alone have also been used in lubrication, and talc has been recommended for improving lubricants. Emulsions made up of the latter are prepared as follows: 3 oz of graphite and 6 oz of talc are thoroughly mixed into 2 gallons of oil and the mixture emulsified in 100 gallons of water.

Lubricants prepared from aqueous graphite suspensions in the usual manner may be improved by lowering the freezing point by the addition of an aqueous calcium chloride solution.⁹⁸

The most important factor in rendering an oil suitable as a lubricant and in improving its characteristics is refining, of which there are several methods.

Sharples⁸⁰ diluted residue-containing lubricating oils, obtained by distillation of crude petroleum, with benzene, cooled and centrifuged to separate the paraffin from the oil. The recovered oil was separated from benzene by steam distillation and found to be highly viscous.

Borodulin,⁸ commenting on the purity of lubricants, states that an admixture of petroleum lowers the ignition point of the lubricating oil, and this decrease may serve as a test for the presence of impurities in an oil. Deutsche Erdöl A.-G.²¹ patented a method whereby stable lubricating oils free from paraffin and brown coal-tar were obtained. Morrell⁶⁸ used sulfuric acid to precipitate suspended pitchy or coke-like substances,

as well as asphaltic materials, from oils to be used as lubricants. About 5 per cent by volume of a sludge acid, obtained from treatment of a cracked distillate with sulfuric acid, is used to treat a cracked residual oil at a temperature of 200° F, the yield of the oil recovered being 80 per cent, with formation of a dense coke-like mass. The liquid was neutralized by filtering through a column of lime, and distilled under diminished pressure to obtain the lubricating oil.

Williams and Russell¹¹⁰ proposed a method for removing metallic soaps from lubricating emulsions. A layer of molten paraffin is poured on a body of lubricating oil emulsion which contains suspended particles of metallic soap. These particles float upward and into the paraffin layer and dissolve in the paraffin.

Mizuta and Toda⁶⁷ claimed that the stability of lubricating oils (naphthenic base oils) was greatly improved by hydrogenation, the best product being obtained by hydrogenating at 250° F for 30 minutes, using as catalysts molybdenum trioxide together with the hydroxides of cobalt, chromium and aluminum, followed by distillation *in vacuo* over 5 per cent acid earth. Not only the stability of the oil was improved, but its color and carbon residue as well. The hydroxides of copper and nickel as catalysts materially aided in improving the stability.

The Standard Oil Development Co.⁹¹ suggests as a suitable antioxidant for lubricating oils, especially of paraffin base, phenyl-cresyl or high molecular alkylated disulfides, mercaptans, and the corresponding naphthyl, anthryl and phenanthryl derivatives. Less than 0.1 per cent is effective.

Spent lubricants may also be purified according to a method described by Stutler.⁹⁵ The used lubricating oil is heated to 225-300° F in the presence of water and an alkaline clarifying agent; is permitted to stand until clarified, distilled in the presence of steam, and then filtered to remove the bleaching agent.

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Chapter 5

Laboratory Methods Used in the Examination of Emulsions

Introduction

In order that emulsions may be treated properly, they are first subjected to a very thorough laboratory examination. A systematic analysis of an emulsion is of great importance, since all other procedures depend on the knowledge of the substance handled. Before selecting the principal methods of investigation that should be applied to the analysis of emulsion systems in order to determine a rational treatment, such as splitting them into their separate phases and recovering the commercially useful oil, etc., a very important factor must be taken into consideration at the well from which the emulsion is obtained. This factor is sampling the emulsion to be analyzed. Estimation of the character of an emulsion and determination of proper methods for its separation depend upon correctness and uniformity in taking samples.

Sampling of Emulsions

If the sample is taken from the top of the fluid column, pure petroleum may be obtained without traces of the emulsion which might be present in the greater part of the production from that well. If the liquid in the well is sampled at a great depth only water is obtained. The most primitive and rarely used device for sampling oil wells is the "bottle method," which was in operation in the Mid-Continent fields in 1924. A description of an apparatus constructed by Butho¹⁴ (a worker in the old Grozny district in Russia) is given in an article by Wischetravsky.¹²⁴ It consists of a support at the end of which is a clamp in which a bottle for taking the emulsion sample is placed, the bottle being about 8 to 10 cm in diameter and 15 to 20 cm in length, not including the neck. The neck of the bottle is fastened to the clamp and the bottle closed with an adjustable cork. The cork is so adjusted that it can be put in tight, without force, yet taken out readily. The cork is fixed to an iron bar which is joined to a lever attached to a support, the opposite end of the lever being attached to a string which passes over a pulley, yet is within reach of the man taking the sample. By pulling the string the cork can be withdrawn, and when the string is released, the cork returns to its original position. A spring arrangement serves to bring the lever to its initial position and close the bottle. In order to get the cork into the neck, a directing part is used. The support has divisions showing to what

depth the device is submerged in the well. After it is submerged to the desired depth, the string is drawn and the cork removed. The bottle is filled with the liquid surrounding it when the cork is withdrawn and the bottle is then closed. After this it can be drawn out with the assurance that no other kind of liquid has entered the container during the sampling other than that taken from a certain depth.

In the United States, well sampling is done with trap bailers. The bottle sampler should be used in wells of much greater diameter than are usually found in the United States. On the other hand a sample, in order to be a true one, must be taken under normal production conditions; otherwise no information as to emulsion characteristics can be obtained. Methods employed for sampling must prevent loss of light fractions and excessive and abnormal emulsification during sampling. Among such methods are the "pressure sampler" and the "copper tube sampler."

A copper tube sampler for sampling crude oils is made up of copper tubing 4 ft long and $\frac{1}{8}$ to $\frac{1}{2}$ in inside diameter; each length is equipped with suitable fittings for joining together in series, if necessary, to reduce the pressure to the desired amount and to make connections to the well head or flow line. The uniform pressure drop through the tube tends to maintain unchanged the relationship or state of combination of the oil and water, so that the sample, when obtained, indicates the state of the mixture at the point of sampling. "Jetting" (quickly reducing the pressure by means of a small opening) of a mixture of oil and water tends, in many cases, to emulsify the mixture so that a sample so obtained does not represent the state of the mixture in the well head or flow line at the point of sampling. This method has been found to be quite satisfactory in ascertaining the state of the mixture of oil and water, or the amount of emulsification, at the point of sampling.* "Bombs" may be used to obtain reasonably true spot samples, but a continuous flow to a sample container or testing device cannot be readily obtained with bombs.

Recently, engineers of the United States Geological Survey, Department of the Interior, at Taft, California, devised a method eliminating emulsification in sampling. Copper tubing $\frac{1}{8}$ to $\frac{1}{2}$ or $\frac{3}{8}$ inch in diameter and about 10 feet in length is connected to a bleeder or other outlet by suitable fittings, and the sample is delivered slowly to the container without agitation and with gradual reduction in pressure. The size of the tubing used depends upon the quantity of gas produced with the oil, and the gravity of the latter. If the volume of gas is sufficient to cause blowing and agitation of the oil stream in the $\frac{1}{8}$ -inch tubing, a smaller size is used. Another sampler, described in Bulletin No. 417,[†] is made of a 4-inch pipe with welded, coned ends, as shown in Fig. 1. The sampler or bomb is fitted with a $\frac{1}{2}$ -inch inlet valve and nipple welded into the side to connect the sampler to the well. Three small nipples with

* Private communication H. G. Barton, U. S. Dept. of the Interior, Geological Survey.

[†] U. S. Bur. Mines, Department of the Interior, Washington, Bull. No. 417 (1939).

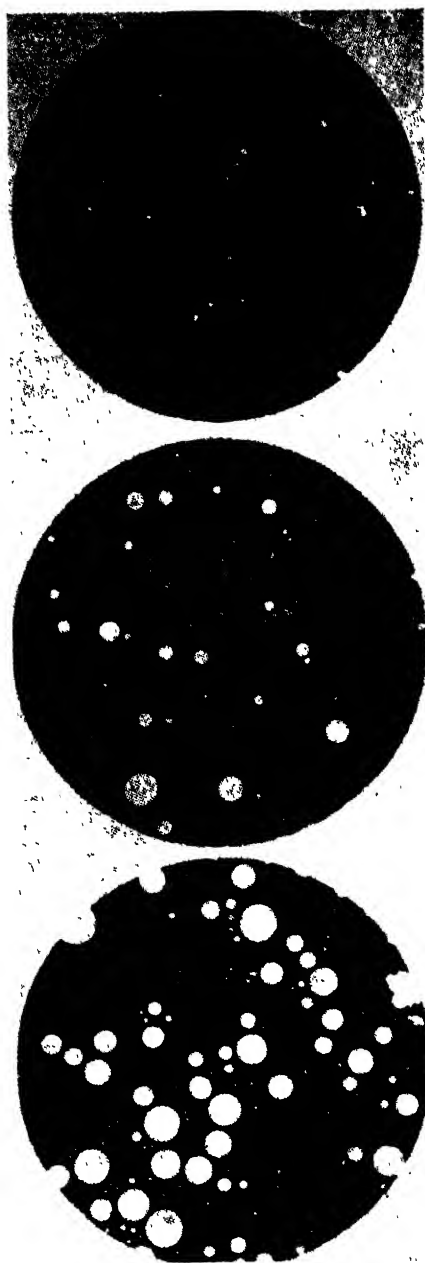
Three types of Bottom-hole pressure sampler are illustrated in "The Science of Petroleum" volume I, page 509 (Oxford), and are classified according to the kind of work which they perform, namely, (1) the flow-through type described by Lindsley⁷⁰ and by Stephenson.¹⁰⁴ In this sampler the chamber in which the sample is to be collected remains open until an upper and a lower valve are closed at the required depth. The fluid in the well flows through the chamber on the way down. (2a) The slow-displacement type, piston-controlled, in which the sample chamber is closed until the inlet valve is opened at the required depth. The sample is slowly admitted to the chamber either by displacement of a piston in the sample chamber as the reservoir fluid enters, or by displacement of mercury from the sample chamber as the reservoir fluid enters, the displaced mercury entering another chamber against a back pressure exerted by compressed gas in the second chamber. (2b) The slow-displacement type, pressure-controlled; and (3) the sudden admission type, in which the sample chamber is closed until the inlet valve is opened at the required depth, the admission of the sample being sudden. No precaution is taken to prevent reduction of pressure on the reservoir fluid.

Moore⁷⁸ described two types of meters for individual well gauging: (1) the vapor-tight model and (2) the open type. In the first model the weighing mechanism is enclosed in a vapor-tight welded and bolted steel tank four feet in diameter and four feet deep. Any gas released from the oil passes freely through this tank into the oil discharge line without affecting the weight of the fluid. In the standard vapor-tight models, the oil is forced through the collecting system under a pressure of about 20 lbs. The open-type meter consists of two triangular buckets, mounted about an axis as a fixed fulcrum, which oscillate back and forth, alternately filling and discharging their contents. The dumping action or oscillation of the buckets is actuated by the weight of the oil in the bucket; and the total number of oscillations is recorded on a register. The open-type meters are generally calibrated to dump a quarter barrel for each complete oscillation, or 75 to 90 lbs while the vapor-tight models dump a half barrel for each complete oscillation, or 150-200 pounds.

The meters working on a gravimetric principle, *i.e.*, weighed through the meter, have an advantage over those operated on the principle of measuring the oil volume. While an increase in temperature effects an increase in volume, it does not change the weight. Gas in solution in the oil has only a slight effect upon the weight of the oil; therefore gas in solution or occluded does not introduce errors.

Microscopic Examination

A microscopic examination is the first step in analyzing an emulsion. When magnified, an emulsion is seen to consist of a number of minute globules of one kind or another suspended in the surrounding medium. In a multiple emulsion, the globules are of two or three kinds intimately



Tight gas-blown emulsion. Oil gravity 28° A.P.I. Water content of the emulsion 24 per cent.

Crude oil emulsion with lower ratio of loose emulsion. Oil gravity 14.5° A.P.I. Water content 24 per cent.

Loose emulsion in low gravity oil, San Joaquin Valley oil, gravity 14.5° A.P.I. Water content 24 per cent.

FIG. 3.

intermingled. (The disperse phase consists of water and oil globules.) Gas and air globules may also permeate the substance and effect a change in their apparent shape and behavior. In some emulsions, due to the amount of mineral matter present in the oil, no specific line of demarcation between single phases can be stated. The appearance of emulsified oil under a microscope is so different from that of crude oil, that the two can not be confused by such an examination.

There are two important requirements for microscopic visibility of the disperse phase (globules) in an emulsion: (1) the difference in the refractive index: invisibility of globules is not a criterion of their absence ("transparent emulsions")⁶⁰; and (2) the diameter of the globules must be greater than the resolving power of the microscope.¹⁷ Hence, if the emulsion contains or consists of very small globules, it may be necessary to employ ultraviolet light or an ultramicroscope to make the particles visible.

Microscopic examination gives no information whatever as to the mechanism of emulsion formation. An emulsion of constant water content, examined under a microscope using low power, shows that the ratio of drop diameter to drop spacing is independent of the drop diameter, *i.e.*, the spacing of the globules of the disperse phase is a function of the percentage of the disperse phase. If more water is added, the water globules gradually become more closely spaced than their diameters. An emulsion of an oil of low specific gravity free from suspended matter is very mobile, whereas an emulsion composed of a heavier oil, irrespective of the amount of suspended matter with the same spacing of globules, is very viscous.

The tendency of an oil to emulsify can also be examined under a microscope. Young¹²⁷ gives an illustrated description of an artificial emulsion prepared by mixing water, petroleum oil, and an emulsifier called "cresoap" (a mixture of soft soap and cresol) which exhibits, under a microscope, flowing and revolving movements resembling those seen in living protoplasm. Young's microscopic observations of emulsification are quoted as follows: "When water touches the oil, the cresoap rapidly forms a broad black wall—the main interface between the oil and the water. As the cresoap dissolves in the water, changing the surface tension, the main interface wriggles and the horizontal and vertical rotating currents emulsify the oil and water in each other. A tough interface is formed by the dissolved soap around each globule of oil. Due to the presence of like charges, globules are repelled, bouncing away from each other like rubber balls.

Scott¹⁰³ investigated the process of petroleum emulsion formation and showed how globules are produced by swirling currents. A petroleum emulsion containing wet clay showed pointed figures which contracted to form globules. The wet clay, being a good adsorbent, is an emulsifier which makes the separation of an emulsion formed very difficult. Fortine,³⁶ in his article on "Oil Treating Methods," illustrates typical crude-oil emulsions by photomicrographs (Fig. 3). A general view of several

(Text cont'd on page 480)



FIG. 4. Elkhills Emulsion.

Emulsion 9.2%, Emulsified Water 8.2%, Free Water 3.0%, Chloride Concentration 0.51N,
Gravity 15.7° B \acute{e} .

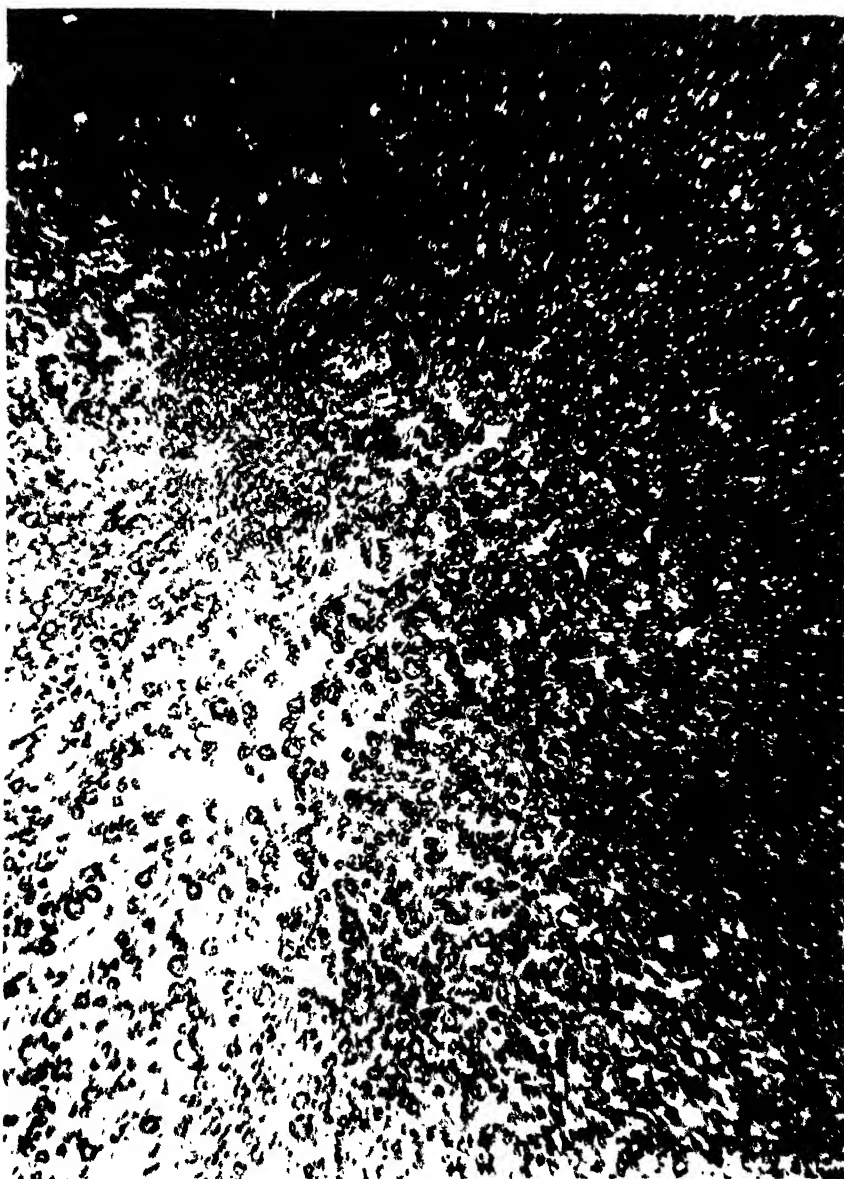


FIG. 5. Buena Vista Emulsion.

Emulsion 0.8%, Emulsified Water 0.2%, Free Water 0.8%, Chloride Concentration 0.593N,
Gravity 25.7° Bé.

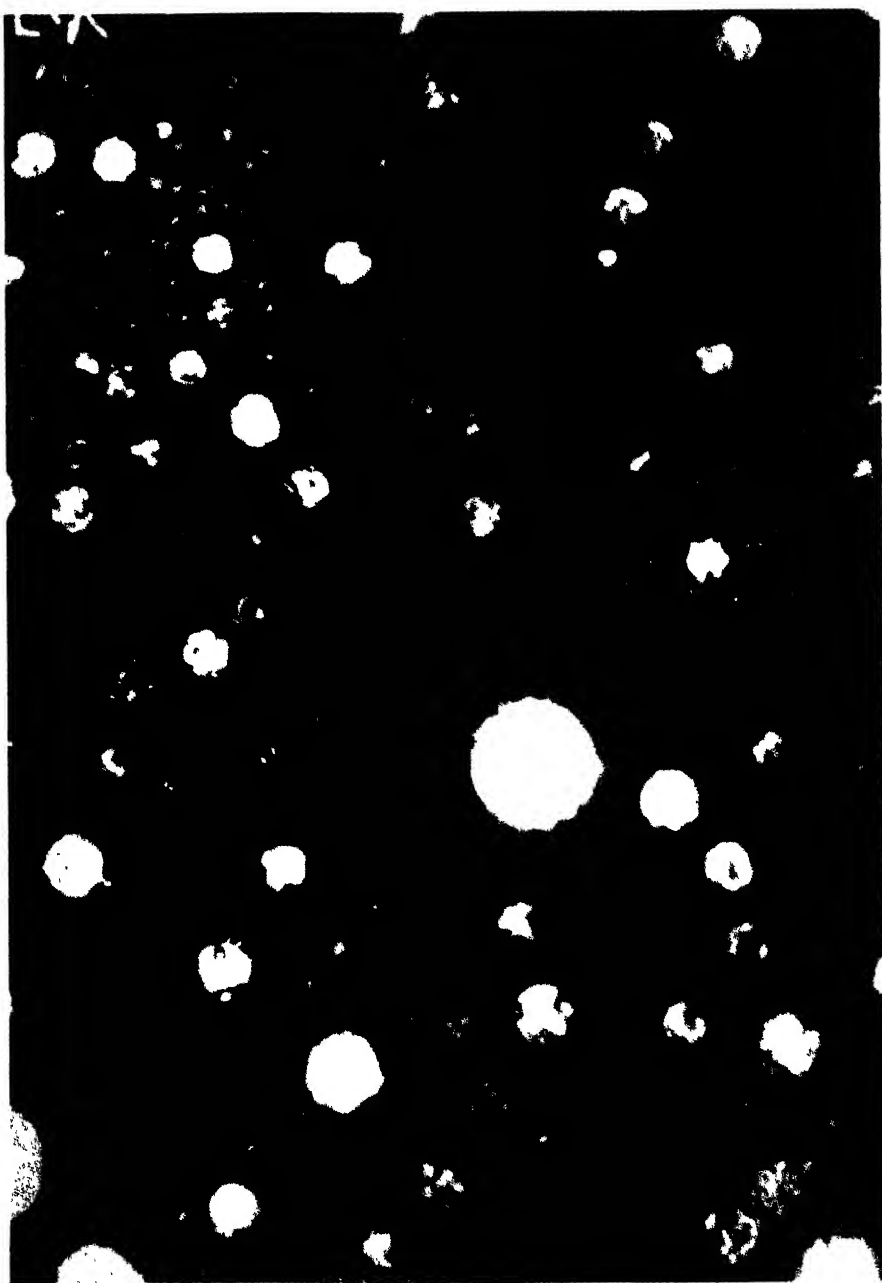


FIG. 6. Coyote Hills Emulsion.

Emulsion 3.8%, Emulsified Water 0.8%, Free Water 0.8%, Chloride Concentration 0.231N,
Gravity 24.3° Ré.

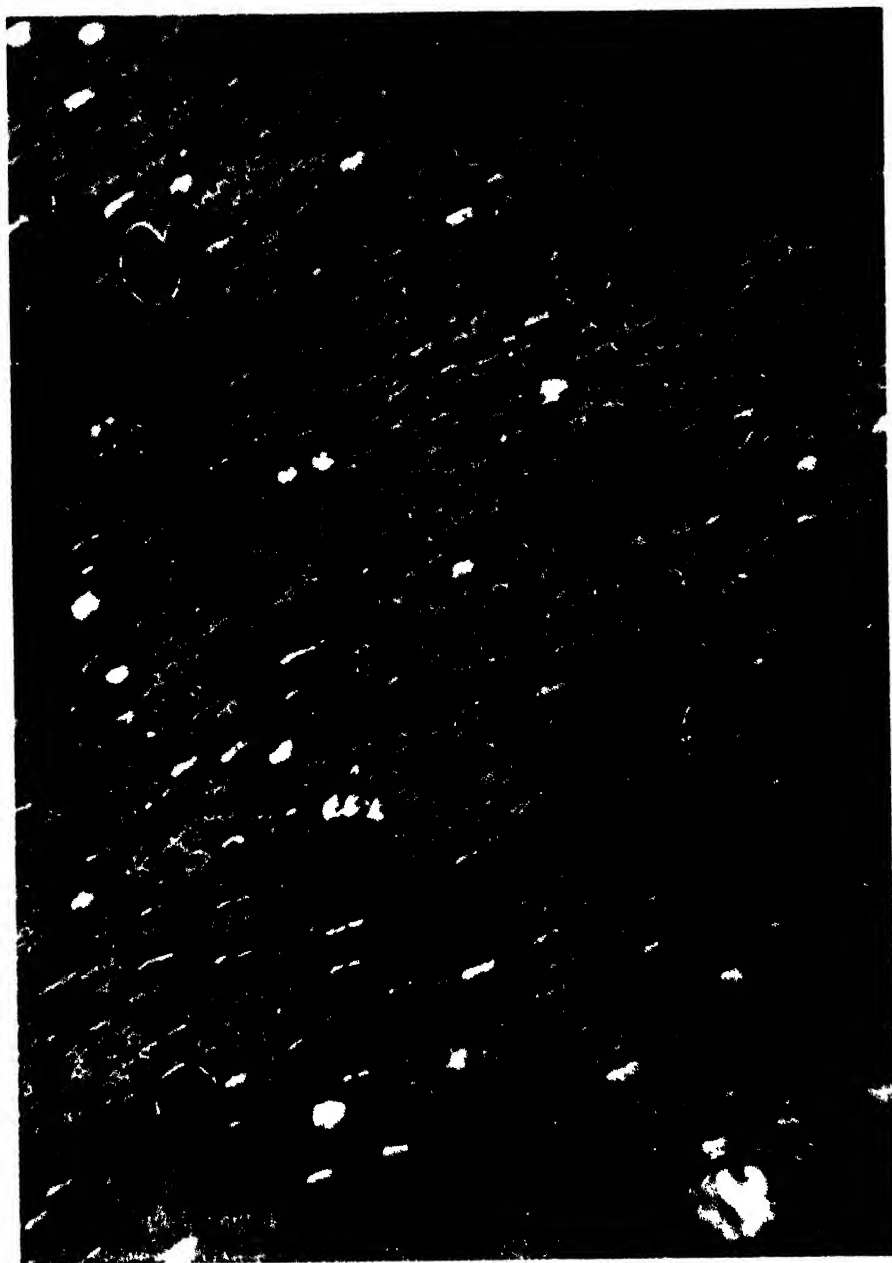


FIG. 7. Casmalia Emulsion.

Emulsion 34.5%, Emulsified Water 24.0%, Free Water 25.0%, Chloride Concentration 0.078*N*, Gravity 11.7° Bé.

emulsions, as seen under a microscope and taken from the work of Abozeid,³ is illustrated in Figs. 4, 5, 6, and 7.

A microscopic method for determining the type of emulsion has been reported by Carriere.^{15,16} This method is based on the same principle as the determination of the refractive index, n of minerals (see Schroeder van der Kolk: "Tabellen zur Mikroskopischen Bestimmung der Mineralien nach ihrem Brechungsindex," 1906). Parallel rays of light passing through a drop of oil in water converge, because the refractive index of oil is greater than that of water. In the case of a drop of water in oil, the rays will diverge. Oil-in-water emulsions, when illuminated with parallel rays of light from the right, will deflect these rays, those from the left entering the objective, while those from the right will be invisible. Therefore, under a microscope, one will see an illuminated border on the right side of the drop, while the other side appears dark. A drop of water in oil gives the opposite effect. Instead of applying rays from one side, insertion of a diaphragm in the shape of a half moon between the concave mirror and the condenser of the microscope is recommended.

Processes taking place in an emulsion, such as coagulation, resulting in the discontinuance of the Brownian movement, can be observed under a microscope. Changes in the distribution of particle sizes by taking number distribution curves in time are important factors in evaluating the stability of an emulsion system.⁷ The character of resolution of an emulsion, under the influence of treating agents, may be roughly estimated. The effect of heat and electric treatment, dilution, etc., upon emulsion systems may be followed from corresponding photomicrographs. Abozeid³ observed the effect of heat (Fig. 8) and of electric treatment (Fig. 9).

In microscopic examinations of emulsions any magnification may be used, depending upon the degree of detail to be observed. Magnifications from about 80 or less to 1800 are usually employed.⁵⁴ With a magnification of 500 or more, the field becomes much smaller, and single areas may be seen in which it is easy to observe Brownian movement.

A polarization microscope is a convenient instrument for the examination of emulsions. By its use admixtures, such as crystals of paraffin, may be differentiated because of their double refraction. S. Berkman,⁸ studying viscous oil-water emulsions, such as pure cedar oil-water, olive oil-water, and Stanolax oil-water under a polarization microscope, observed between crossed Nicol prisms the following phenomenon: A few of the oil droplets in the polarizing plane appeared as spheres having four dark spots at the edge of the oil droplet, and between the dark cross so formed, bright spots of the droplet edge were outlined. The edges of the dispersed oil droplets of different sizes and shapes exhibit polarized light with varying intensity and a variety of colors. The colors produced, as well as the intensity of the polarized light displayed, are visible only at the edge of the oil droplet and disappear in the direction of the center of the droplet. The cross formation at the edge of an oil droplet in the emulsion observed is due to polarized light, and must be

(Text cont'd on page 483)



FIG. 8. Elkhills Emulsion.

Heat Effect on Emulsions. Temperature Applied 38.5°C. Time of Exposure 40 sec.



FIG. 9. Elkhills Emulsion.

Electrical Treatment of Emulsions. Voltage 110; Time of Test 5 sec.

regarded as the result of a "surface polarization." Whereas ordinary double refraction is due to the presence of a double refracting substance inside of an oil droplet and corresponds to internal polarization of a crystalline substance, in the case of non-crystallized substances, such as emulsions, the polarization occurs at the edge of the oil droplet, which is the boundary surface with respect to the water medium. In the case of emulsions, the surface colors are produced by surface refraction, and the change in colors is due to a change in the angle of incidence of light. This change in colors occurs in the vertically polarized light, the colors themselves being the result of the reflection of a thin layer at two boundary areas where the reflected rays of light interfere. From the observed "surface polarization" phenomenon occurring in certain viscous emulsion systems, the following requirements for its existence may be enumerated: (1) a great difference in the refractive indices of oil droplets and the surrounding dispersion phase; (2) a definite kind of polarization of the reflected light; (3) a definite magnitude of the angle of incidence of light. Regular, round droplets exhibit the best polarizing effect.

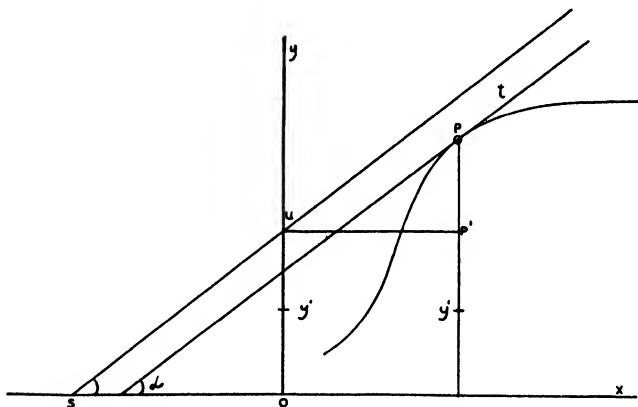


FIG. 10. Construction of a Derivative Curve
(S. Berkman).

A new type of Leitz microprojection equipment fitted with a special collimator of strong light-transmitting power is very useful in obtaining number distribution curves.⁷ By means of a projection prism above the ocular, the image obtained in the microscope is projected on a screen of millimeter graph paper attached to a wall opposite the projection prism. The distance of the screen from the microscope stand is chosen so that each millimeter of the graph paper corresponds to one micron (micrometer calibration). In the microscopic examination of an emulsion, special precautions should always be taken when using an arc lamp as the source of illumination. To counteract the influence of heat, cells containing heat-absorbing solutions (such as a solution of ammonium ferrous sulfate to which a few drops of sulfuric acid have been added to prevent

(Text cont'd on page 486)

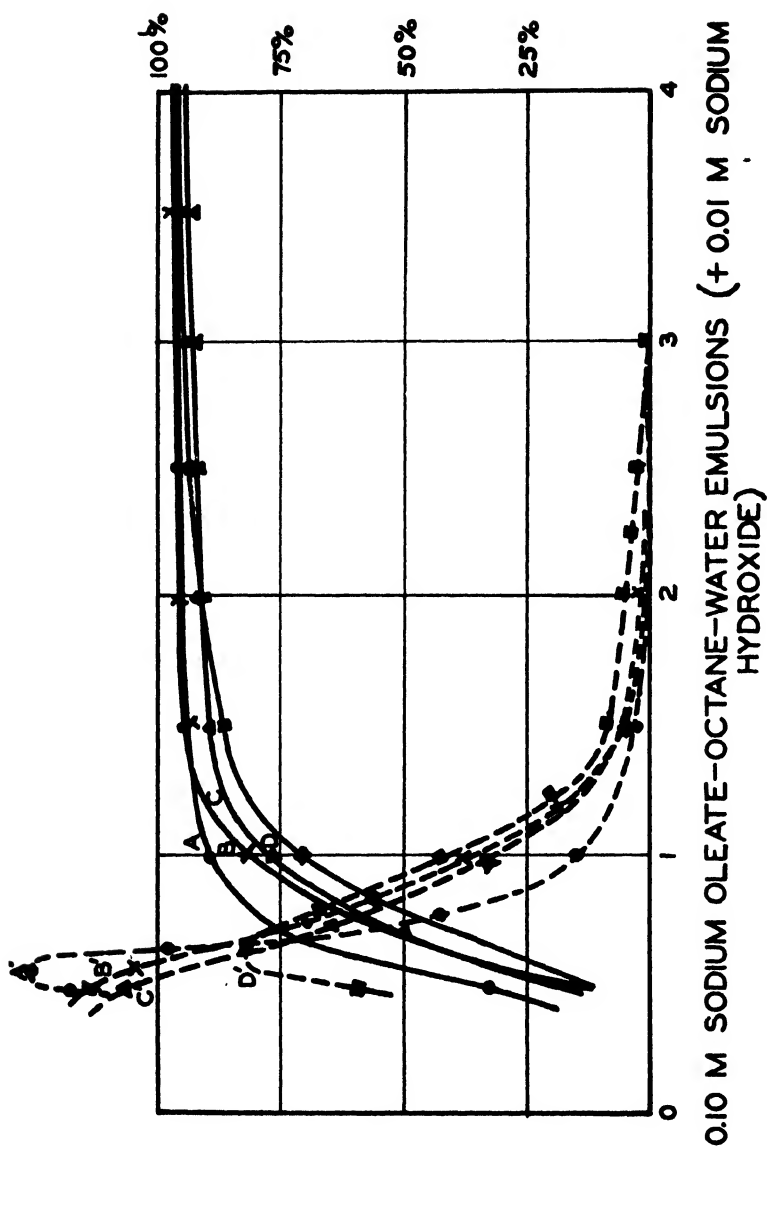


Fig. 11a.

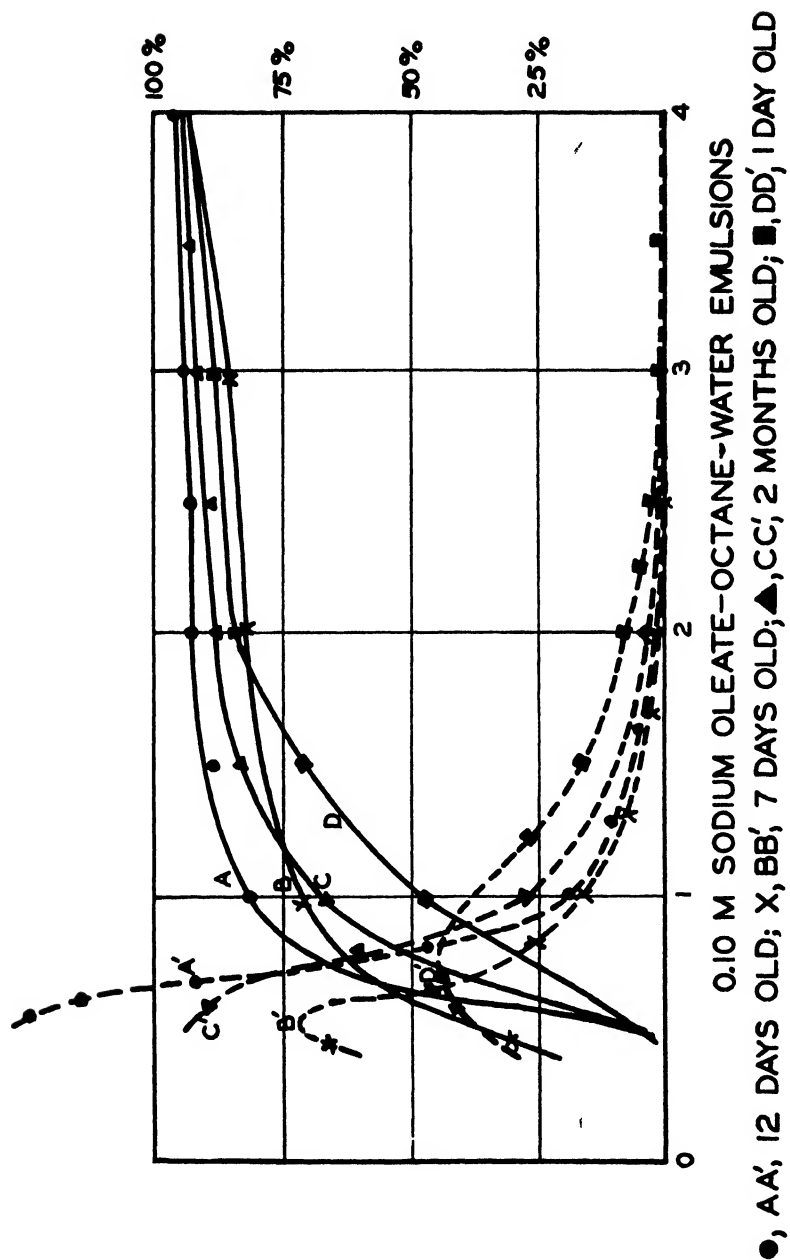


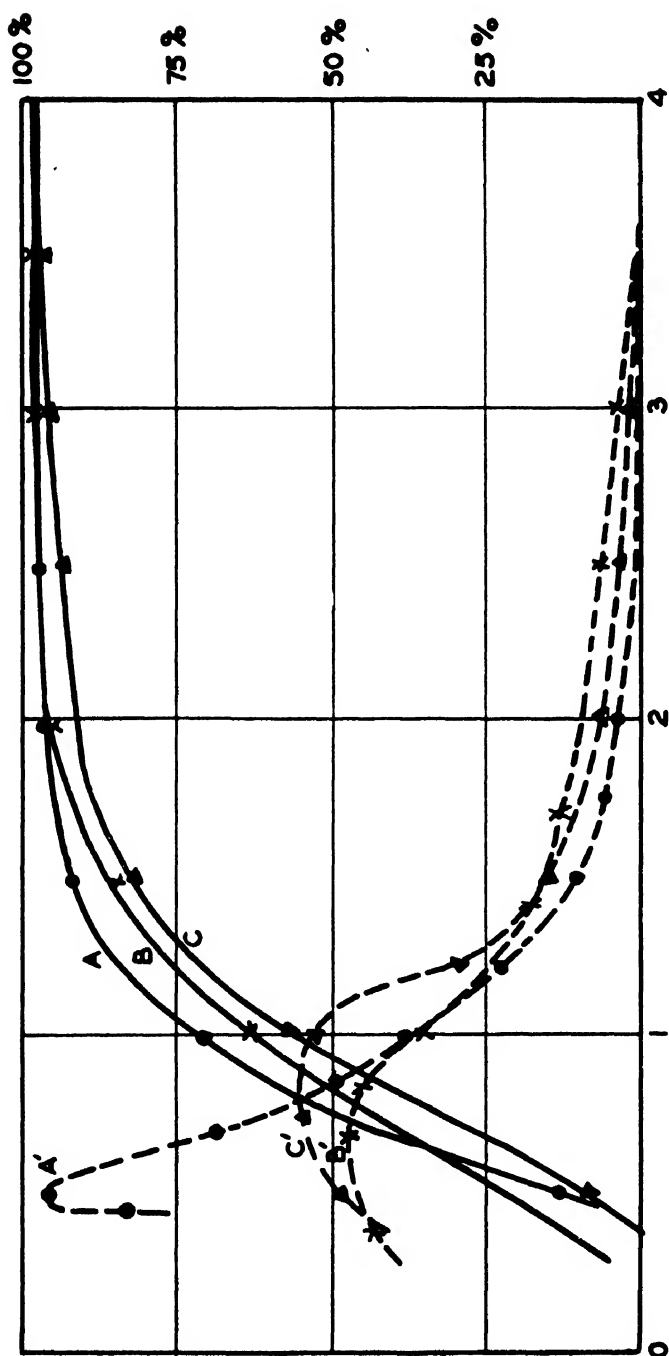
FIG. 11b.

oxidation on exposure to air), special glass screens, and cooling systems are recommended. In the case of slides which cannot be closed tightly, use of adsorbing cells to prevent evaporation and drying of the emulsion is advisable. Adsorbing cells are ordinarily used to eliminate heat effects, such as induced thermal agitation in the specimen; but in ultramicroscopic practice they also prevent thermal distortion of the dark-field condensers.

The kinetics of changes in emulsion systems with time cannot be followed from number distribution curves alone, because it is necessary to pursue small rates of changes in the physical mass; therefore a mathematical analysis must be applied. S. Berkman⁷ devised a method for measuring the stability of emulsions by deriving mathematically the differential curves for the corresponding integral curves obtained by plotting directly the distribution of sizes of oil droplets and the corresponding percentage of droplets. In the evaluation of the derivative, $y' - \frac{dy}{dx}$, where the function is known analytically, differential calculus or a graphical method must be used. Geometrically, the procedure consists in applying the principle that the ordinate of the derivative curve at any point $P'(x,y)'$ is equal to the slope of the integral curve at any point, that is, of the tangent at the corresponding point of the integral curve. The practical construction of the derivative curve is shown in Fig. 10. Point $S(-2,0)$ is chosen at a convenient distance to the left of the axis y , and a line parallel to the tangent is drawn for each point of the integral curve. This parallel cuts the ordinate axis at the point U . Since SU forms with the axis x the same angle α as the tangent t , then $OU = tg\alpha = y$, and the point U projected horizontally on the ordinate from the point P cuts it at P' , which is the point on the derivative curve corresponding to the point P of the integral curve. Since $Y' = 1/a \int y \cdot dx$, then $dy/dx = 1/a Y$. The slope of the integral curve at any point is proportional to the ordinate of the derivative curve at the corresponding point. Derivative curves for the integral curves constructed in this manner are presented in Figs. 11, 12, 12a, and 13.⁷

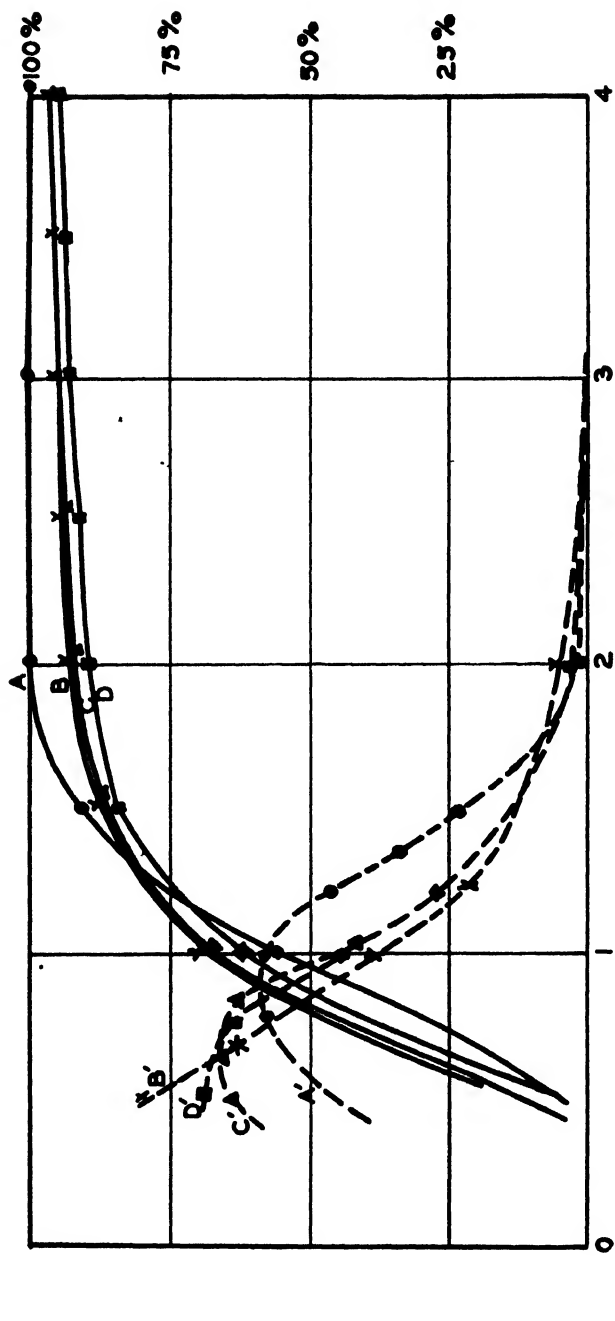
By means of an integragraph, Bailey, Nichols and Kraemer⁴ devised a method of calculating the relation between the optical absorption coefficient of a colorless emulsion and the radius of the particles from a series of "weight optical" distribution curves determined with a Svedberg low-speed ultracentrifuge. A particle size distribution may be expressed as a relationship between concentration and particle size, dc/dr and r , where dc/dr is proportional to the weight of particles having a radius between r and $r + dr$. The ultracentrifuge gives the relation between the absorption coefficient $d/(KC)/dr$ and the radius r , whereby K is the apparent absorption coefficient of a suspension of particles with radius r . For a suspension of colorless particles in a colorless medium, the "absorption" is entirely due to scattering, and the absorption coefficient provides a measure of the light-scattering power of the suspension. The relation

(Text cont'd on page 491)



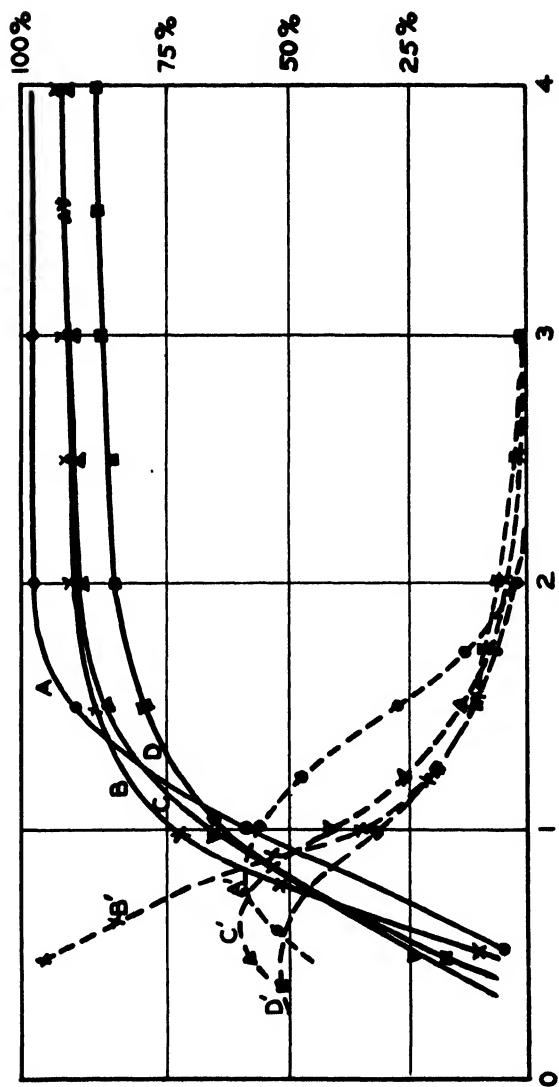
0.005 M SODIUM OLEATE-OCTANE-WATER EMULSIONS
 ●, AA', 3 DAYS OLD; X, BB', 1 MONTH OLD; ▲, CC', 15 DAYS OLD

FIG. 12a.



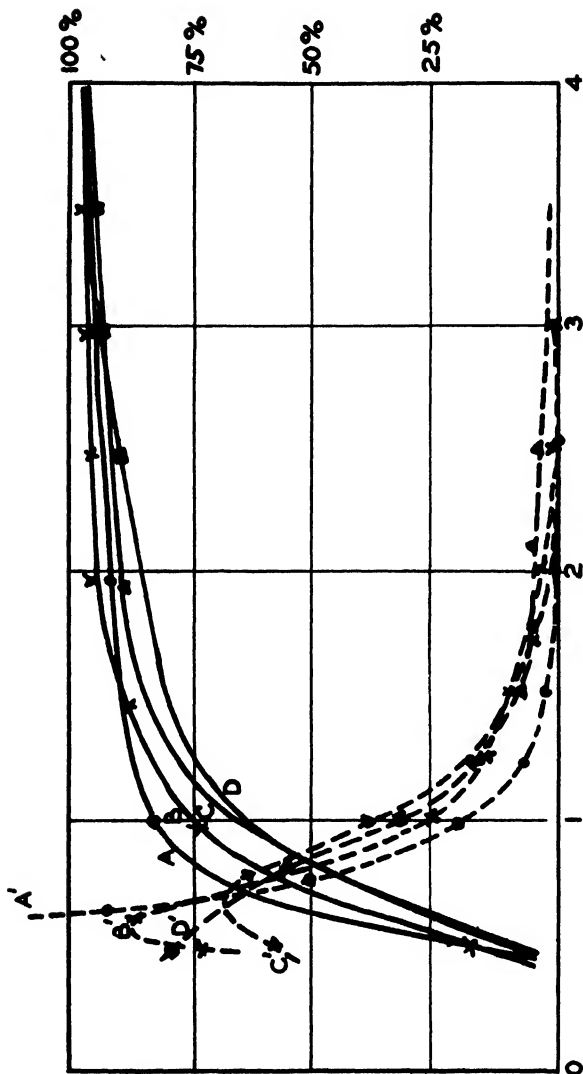
OCTANE-WATER EMULSIONS (TWO MONTHS OLD)
 ●, AA', 0.01 M SODIUM OLEATE; X, BB', 0.10 M SODIUM OLEATE + 0.01 M SODIUM HYDROXIDE; ▲, CC', 0.05 M SODIUM OLEATE; ■, DD', 0.10 M SODIUM OLEATE

FIG. 12b.



0.01 M SODIUM OLEATE-OCTANE-WATER EMULSIONS
 ●, AA', 2 MONTHS OLD; X, BB', 3 MONTHS OLD; ▲, CC', 15 DAYS OLD; ■, DD', 2 DAYS OLD

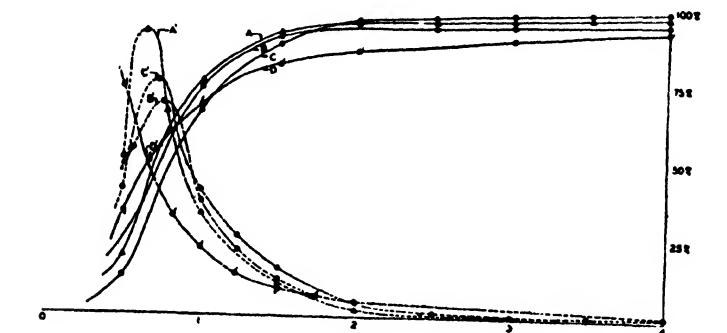
FIG. 12c.



0.05 M SODIUM OLEATE-OCTANE-WATER EMULSIONS
 ●, AA', 12 DAYS OLD; X, BB', 7 DAYS OLD; ▲, CC', 2 MONTHS OLD; ■, DD', 4 DAYS OLD

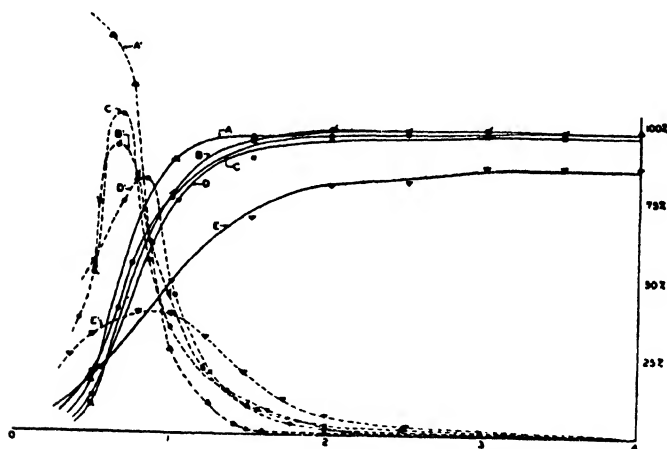
FIG. 12d.

between $d/(KC)/dr$ and r is called the "weight optical" distribution. The light-scattering power of a series of emulsions of constant particle size distribution, but different refractive indices, is reported in terms of



STANOLAX-WATER EMULSIONS

Δ , AA', 0.10 *M* sodium oleate, seven days old; \circ , BB', 0.10 *M* sodium oleate + 0.05 *M* oleic acid, five years old; \bullet , CC', 0.10 *M* sodium oleate, forty-one days old; ρ , DD', 0.10 *M* sodium oleate, four years old.



STANOLAX-WATER EMULSIONS

Δ , AA', 0.05 *M* sodium oleate, twelve days old; ρ , BB', 0.05 *M* sodium oleate, seven days old; \circ , CC', 0.10 *M* sodium oleate, seven days old; \blacksquare , DD', 0.005 *M* sodium oleate, four days old; ∇ , EE', 0.005 *M* sodium oleate, twelve days old.

FIG. 13.

apparent absorption coefficient K . A general relationship connecting the apparent absorption coefficient with the particle size, the refractive indices of particles and the medium, as well as the wave-length, may be deduced by means of the integraph. The integraph devised for this purpose is

based on the principle of a two-dimensional moment balance. If the "weight optical distribution" is expressed by the equation:

$$d(KC)/dr = fn(r)$$

and the variation of the absorption coefficient K with r by the equation

$$1/K = F(r)$$

then

$$\int_{r_{\min}}^{r_{\max}} fn(r) \cdot F(r) = 1$$

Each weight optical distribution is represented by a particular $f(r)$, and from a series of integral equations equal in number to the experimentally determined weight optical distribution $F(r)$ is calculating.

The interfacial film involved in emulsification is not colloidal in nature as a rule, and the ultramicroscopic droplets of emulsified oil do not contribute largely to the total area of the oil-water interface. Sometimes both the aqueous phase of an emulsion and the soap solution from which emulsions are prepared are investigated in a slit ultramicroscope (Leitz). Usually the colloidal particles present in the original soap solution are counted and subtracted from the count made on the emulsion. If the particle volume in emulsions is known (modified Babcock test), the average particle diameter may be calculated. A quantitative ultramicroscopic examination involves determination of the number of ultramicros in 1 cm³ of the disperse system and calculation of the average particle diameter, assuming a definite form for the ultramicroscopic particles. In principle, the method consists in determining the average value, m , of the number of particles by counting those showing Brownian movement. If, by a concentration determination, the gram weight, G , of the disperse phase is known, then the weight of a single particle is G/m (the particles or globules are assumed to be of the same size, and the system monodisperse), and the particle volume, $G/(M.S)\text{cm}^3$, where S is the specific gravity of the particle. By assuming the particles to be uniform and cubic,* with edge length (d), then d may be considered as the par-

ticle diameter and therefore equal to $\frac{\sqrt[3]{\bar{v}}}{M.S}$. Other methods may be used

in determination of particle diameter, namely, calculating it from the intensity of the reflected light. However, this method has little practical application.

Test Methods

Methods of testing emulsions and their components are either physical or chemical in nature. Some of the tests characterize the properties of the material tested with respect to the service it renders; others

* It is desirable to consider the particles spherical in form rather than cubic, as this is true in practically all emulsion systems.

indicate the degree of refining; and, finally, there are tests which comply with certain specifications or requirements.

A liquid in the form of a freely suspended drop and upon which no external force exerts an influence assumes the form of a sphere. The tendency to acquire the smallest specific surface is designated as the action of tension, and originates at all boundaries between phases. Surface tension exists on the surface of liquids or solid bodies, and interfacial tension operates at the boundaries between solid, liquid, or gaseous phases. Surface tension is $\sigma = \text{work/surface}$, and when expressed in the CGS system, the unit is $1 \text{ erg/cm}^2 = 1 \text{ dyne/cm}$. It is the interfacial tension which plays a significant role in the case of disperse systems, for the smaller the interfacial tension between the disperse part and the dispersion medium, the less boundary energy will be required and the more effective will be the dispersion process. This relationship is especially pronounced in the emulsification of two liquids having a small interfacial tension. In order to facilitate emulsification of oil in water, substances decreasing interfacial tension are added. The molecular theory of boundaries is related to cohesion, adhesion, polarity, and capillarity. Surface tension originates in the cohesion of molecules. On the inside of a liquid, where a molecule is surrounded by other molecules, the cohesion tendency is saturated; but at the surface of a liquid, where a molecule touches others only in the liquid side and faces free atmosphere on the other side, the cohesion tendency is less saturated, and work, corresponding to the value of cohesion, must be applied in order to bring the molecule to the surface. This work, identical with surface work, is equal to the product of surface tension σ and surface f . A liquid/liquid or a liquid/solid boundary originates when both phases form free surfaces (against vacuum), and when these are brought into contact. In the first stage of this process, work against the cohesion of the molecules must be applied; in the second stage, work is gained in the form of adhesion between the two phases. The total boundary work ($\sigma_{a,b}$) is, therefore, composed of cohesion ($\sigma_a + \sigma_b$) and adhesion ($A = \sigma_a + \sigma_b - \sigma_{a,b}$). Adhesion values of organic liquids toward water show a relationship with respect to the molecular properties of the liquids. The adhesion of normal paraffins is comparatively small, 36-48 erg/cm²; but when hydrophilic atomic groups, such as hydroxyl and carboxyl, are present in the molecule, adhesion is markedly increased. In the first place, it is a function of the end group and, in the second place, it depends on the size of the remaining part of the molecule. This indicates an orientation of molecules in the surface whereby the hydrophilic end group touches the water, while the remaining part is directed toward the interior of the liquid.

The hydrophilic end groups, which increase the adhesion toward water (likewise the solubility in water), are polar, *i.e.*, possess an electric dipole moment, while the remainder of the molecule is non-polar. The hydrophilic character of polar end groups arises chiefly from the electrostatic adhesion of strong polar water molecules. Molecules of liquid containing hydrophobic groups in addition to hydrophilic atomic groups orient them-

selves in the interface toward water in such a manner that for the most part the hydrophilic groups touch the water. Likewise, solutions consisting of molecules of various cohesion and adhesion values orient themselves so that those with weak cohesion and strong adhesion stand at the interface. The accumulation of atomic groups, as well as of molecules in the boundary, is parallel with a decrease in the interfacial tension, such atomic groups and molecules being designated as "capillary active." The accumulation of "capillary active" substances at the interface is a diffusion process and requires a certain period of time; the final value of interfacial tension is established gradually.

Typical "capillary active" substances in aqueous solution are soaps. A concentration of one per cent suffices to decrease the surface tension against water to one-half; against oil, the decrease is still greater. Proteins, dyestuffs, etc., are examples of colloids which exhibit strong capillary activity.

Among molecularly dispersed capillary active substances are those which contain in the molecule a hydrophilic atomic group (bringing about dissolution), in addition to a capillary-active hydrocarbon group, for example, fatty acids, alcohols, urethanes, etc. Traube's rule shows that capillary activity in the homologous series of alcohols, as well as in other homologous series, increases with an increase in chain length. Therefore, in order to obtain the same decrease in surface tension, it is necessary that each successive higher member of a homologous series be taken in about one-third of the concentration of the previous member, which is smaller by one CH_2 -group. On the contrary, hydrophilic substances, such as inorganic salts, are inactive; they increase the surface tension.

Surface-tension Measurements

The following methods for determining surface tension are discussed in some detail:

The Capillary Rise Method. As a measurement of interfacial tension, this method may also be used for measuring the surface tension of molecularly and colloiddally dispersed systems. Liquids rise when they are able to wet the walls of a capillary tube. As the liquid tends to spread over the whole inside of the tube, the surface tension has the tendency to decrease this surface with respect to the gas space, drawing the liquid to the top. An equilibrium is finally established between the force, the surface tension, and the weight of the lifted liquid in the capillary. If the diameter of the capillary is $2r$, then the force acting is $2\pi r\sigma$ (σ — surface tension), and the weight of the lifted liquid $r^2\pi hgd$, where h denotes the height, and d , the density of the liquid. Therefore, in the equilibrium state: $2\pi r\sigma = r^2\pi hgd$, and $\sigma = \frac{g}{2}rhd$. This equation indicates that the higher the capillary rise the greater the surface tension.^{51, 94, 116, 121}

Ferguson and Dawson,³⁵ as well as Edwards,³¹ used a manometer to measure the pressure required to force a liquid down to the lower end of

a capillary tube immersed vertically in it. If h_1 is the manometric pressure; h_2 , the depth of immersion of the tip in the liquid; d_1 , the density of the manometric liquid (paraffin); d_2 , the density of the liquid examined; r , the internal radius of the tube at the tip, and σ , the surface tension, then the latter is expressed as follows:

$$\sigma = g \frac{r}{2} (d_1 h_1 - d_2 h_2) + g d_2 \frac{r^2}{6}.$$

Usually, a simple capillary tube, or a U-tube with tubes of different diameters, is immersed in the liquid and the level difference accurately read, using a cathetometer. The advantage of this method is that a capillary of uniform bore is not required, and it is only necessary to know its diameter at the point to which the meniscus has been adjusted.

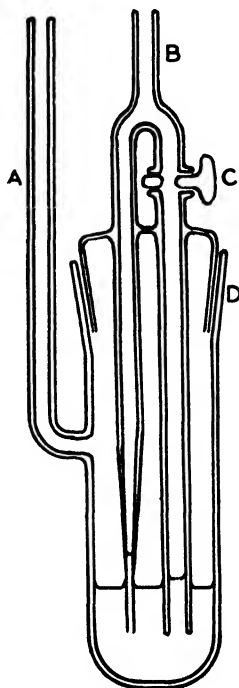


FIG. 14.

The Bubble Pressure Method. This method operates on the principle that surface tension is due to the relationship between the excess pressure p in dyne/cm² necessary to overcome capillary pressure and the capillary radius r , according to the equation: $\sigma = 1/2pr$ dyne/cm. A narrow capillary with sharp edges at the end is immersed in the liquid to a specific depth. By excess pressure an air bubble originates, and the pressure at which the bubble tears off is measured.⁶³

To eliminate hydrostatic pressure, Sugden employed an apparatus (Fig. 14) consisting of two capillaries of different diameters immersed in

the liquid to the same depth. Thus, only the buoyancy of bubbles has to be considered, which increases the excess pressure by $2/3dr$. If r_1 and r_2 are the radii of the capillaries and p_1, p_2 the manometrically measured bubble pressures, then the surface tension is calculated as

$$\sigma = A[p_1 - p_2 - 2/3d(r_1 - r_2)],$$

the constant A being determined by calibrating the apparatus with a liquid of known surface tension. (The capillary radii should not exceed 1 mm).

The Curvature Method. This is based on the fact that a liquid under no strain tends to form a surface nearly globular in shape, which occupies a minimum surface. Thus the surface tension may be calculated from the curvature of the surface formed. A meniscus of a liquid of known diameter is produced and an object of known size is allowed to give its mirror image in the liquid surface. From the size of the object and of its image, which is measured by a microscope, and the distance between the two, the radius of curvature of the surface is obtained.

The Method of Vibrating Jets is based on the study of drop-curvature. A liquid permitted to flow from an elliptic opening does not form a cylindrical jet, but one with constrictions, indicating a wave curve in the cross-section. Rayleigh^{93a} showed that this phenomenon of an oscillation about the position of equilibrium is due to surface tension; and he applied the general equation for isochronous oscillation:

$$\frac{\theta^2}{\pi^2} = \frac{\text{moment of inertia}}{\text{directive force}};$$

where θ is the period of oscillation. The moment of inertia proportional to the mass is therefore proportional to the density of the oscillating liquid and depends also upon the shape of the opening. The directing force is a function of surface tension and increases in proportion to it;

hence; $\frac{\theta^2}{\pi^2} = A \frac{\rho}{\sigma}$; where A is a constant, and ρ and σ are density and surface tension, respectively. If we consider that $\theta = 1/n$, and $n\lambda = v$ (n is the frequency; λ , the wave length, and v , the velocity of the falling liquid), then

$$\sigma = \frac{A\pi^2\rho V^2}{2}$$

With a given velocity of efflux, σ is greater, the greater the density and the smaller the wave-length. The final formula deduced by Rayleigh is as follows:

$$\sigma = \frac{4\pi^2 r^3}{V^2 - V} \frac{\rho V^2}{\lambda^3}$$

where r denotes the radius of the circle of equilibrium and is a number which depends upon the shape of the opening, being 2 for an elliptical

opening, 3 for a triangular one, and so on. It is not easy to determine r exactly, and the method is used for relative measurements with the same efflux orifice. The wave-length λ is determined by photographing the jet and then determining the distance between loops or nodes. The velocity of efflux v is equal to $\sqrt{2gh}$ (Torricelli's Law).

The Method of Vibrating Drops, used by Lenard,^{69a} is similar to the foregoing in many respects. If drops fall from a tube under suitable conditions, at the moment of separation from the orifice, they have a form which is not strictly spherical but ellipsoidal, because of the action of gravity. In falling, they oscillate about their form of equilibrium. By photographing a drop at different points of its fall, the period of oscillation is determined. The formula for the surface tension is expressed as follows:

$$\sigma = \frac{3}{8} \frac{W}{\theta^2}$$

where W is the weight of the drop and θ the period of oscillation.

The Method of Surface Waves (Ripples) serves to determine surface tension and involves W . Thomson's formula:

$$\sigma = \frac{1}{2\pi} \rho n^2 \lambda^2 - \frac{g \lambda^2 \rho}{4\pi^2}$$

Surface waves (ripples) are generated upon a liquid surface in the form of waves advancing linearly if a glass plate affixed to one of the prongs of an oscillating tuning fork dips 1-2 mm into the liquid. Likewise, standing circular waves may be generated upon a liquid if the points of the tuning fork dip 1-2 mm into the liquid. The ripples are photographed and measured.

The Method of Adhesion Plates and the Ring Method. These involve measuring the force necessary to tear a plate or a metal ring from the surface of the liquid tested. Usually a platinum-iridium ring made of wire (the size of which depends on the size of the ring; rings having radii from 0.4 to 0.8 cm were made from wire with radii between 0.009 and 0.05 cm) is suspended on an arm rigidly fixed to a fine steel wire (0.25 mm in diameter) secured at both ends in torsion heads, each of which is driven by a worm-gear arrangement. To separate the plate or ring from the liquid, a force proportional to the surface tension must be applied. The formulas for determining surface tension by the ring method are:

$$(1) \quad ST = P \left(\frac{V}{P} \right) = F \times P$$

where ST is the surface tension, F the correction factor, and P the maximum pull on the ring.

$$(2) \quad \frac{V}{P} = f \left(\frac{R^2}{V}, \frac{R}{r} \right)$$

where R is the radius of the ring, V the volume of the liquid raised above the surface due to a pull on the ring, and r the radius of the wire of the ring.

$$(3) \quad \frac{R^3}{V} = \frac{R^3 g \rho}{2cP}$$

where g is the acceleration of gravity, ρ the density of the liquid, and $c = 2\pi R$.

Correction curves and tables, in which values of R^3/V for various R/r , together with the appropriate correction factor F are given, may be found in Harkins' article.^{53a}

Any accurate balance may be used for carrying out these measurements. The torsion balance by Lecomte du Nouy is known as the du Nouy tensiometer.⁵³ In this mechanism the ring is balanced in the air by adjusting the torsion of the wire by means of the back adjustment and keeping the front torsion head set on zero, when the ring is lowered until it touches the surface of the liquid. The clockwise or counter-clockwise movement of a vernier moves the ring down when water has the lower density of the two liquids investigated; up in the opposite case. The force per centimeter is read directly from the vernier on the torsion head when the interfacial film is broken by the ring. The ring method is distinguished by its simplicity, speed, and accuracy. In addition, the rate of change in surface tension with age on a static surface can be determined by this method, and this is of vital importance in the study of surface phenomena.

The theory of this method is discussed in several works.^{38, 53, 69} Fahrenwald⁵³ modified the ring method by replacing the ring with a thin metal knife edge, whereby the pull of a film of liquid is measured.

The Drop-Weight Method is most frequently used for determining the relative surface tension. In this method the liquid is allowed to drop from a pipette having a polished circular orifice, and either the weight of a number of drops or the "drop number" for a given volume flowing out is determined. Tate's law ($w = 2\pi r \sigma$) that the weight of a drop of liquid, w , when detached from a tube is proportional to the surface tension, σ , and the periphery of the tip of the tube, $2\pi r$, is not in agreement with the theory of capillarity. Lohnstein's many investigations^{70a} led him to formulate this equation:

$$Mg = 2\pi r \sigma F\left(\frac{r}{a}\right)$$

where $Mg = w$; $a = \sqrt{\frac{2\sigma}{d}}$, and d is the density; F denotes an arbitrary function. In a table giving the range of values for $\frac{r}{a}$ usual in experimental work, $F\frac{r}{a}$ is constant (about 0.62).

Harkins and Brown⁵¹ considered the fact that the weight of a drop is also a function of its shape. The latter depends on the ratio between two linear dimensions of the drop, r and l , since a drop does not become detached from the exact edge of a tip, but forms a neck a little below the edge and then detaches; its weight is less than the ideal weight. By substituting the cube root of the volume of the drop for l , the actual weight of the falling drop is expressed by the equation:

$$Mg = 2\pi r \sigma F \left(\frac{r}{V^{1/3}} \right) \text{ and } \sigma = \frac{Mg}{2\pi r F (r/V^{1/3})}$$

These investigators prepared a table of corrections for the drop-weight surface tension method in which F , necessary for the calculation of σ , may be found.

Harkins and Freud,^{52a} studying hanging and detached drops from a horizontal circular tip, concluded that the method of Harkins and Brown is empirical in regard to relations existing between the size of the drop

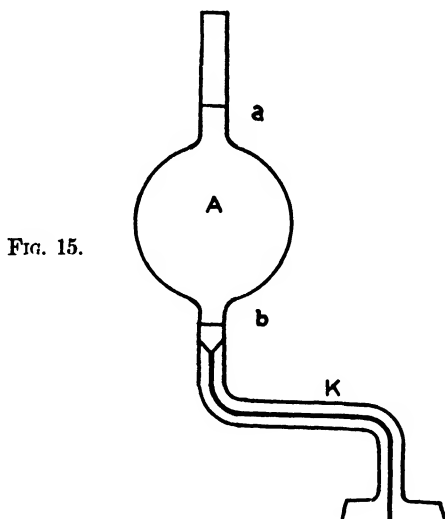


FIG. 15.

and the known constants of liquid and tip. The speed of formation of a drop has been recognized as an important factor. Usually the speed of drop formation should not exceed one drop in 8-10 seconds. A speed of drop formation greater than this introduces dynamic effects which vitiate completely the accuracy of the measurement. The number of drops formed at a slow rate of flow from a volume of liquid contained in A (Fig. 15), between marks a and b , is determined by means of Traube's stalagmometer. A capillary tube, K , is inserted before the efflux orifice in order that the drops may be formed more slowly.

Interfacial-tension Measurements

The same methods used for surface-tension determinations may be employed in measuring the boundary tension between two different liquids. If, for instance, the drop-weight method is used, the interfacial tension is calculated from the equation:

$$\sigma = A \frac{m}{r} \frac{d_1 - d_2}{d_1}$$

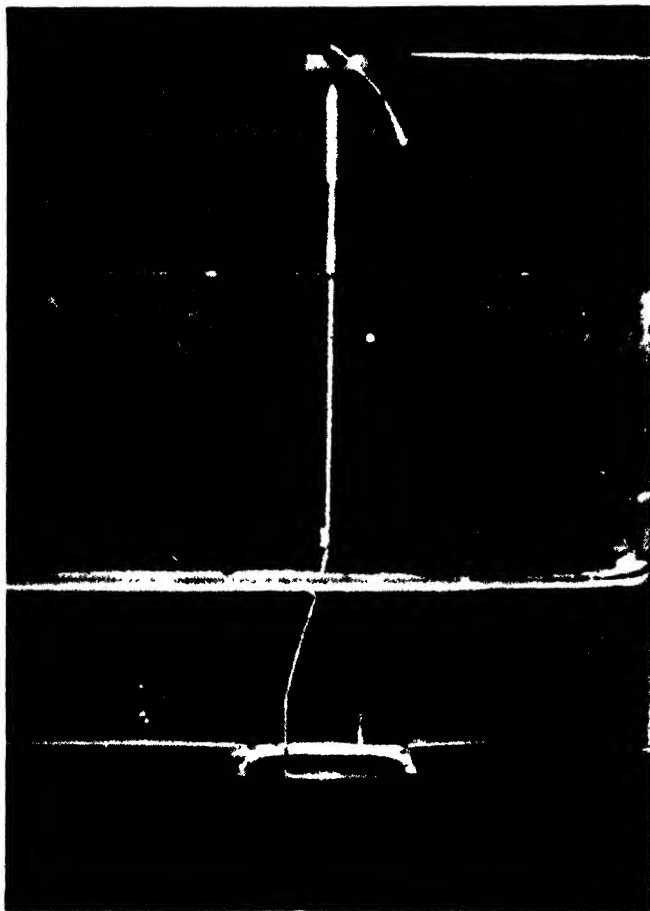


FIG. 16.

where d_1 and d_2 are the densities of the two liquids. The bubble pressure method or the tearing off method are also suitable. Air, or a suitable inert gas, such as nitrogen, is forced into the capillary tube so that bubbles escape at the end of the tube. From this is determined the

maximum pressure which can be reached with a slow escape of bubbles. If p is the maximum pressure; r , the radius of the capillary, and ρ the density of the liquid, then, according to Schrödinger,^{108a}

$$\sigma = \frac{r}{2} p \left\{ 1 - \frac{2\rho r}{3p} - \frac{1\rho^2 r^2}{6p^2} \right\}$$

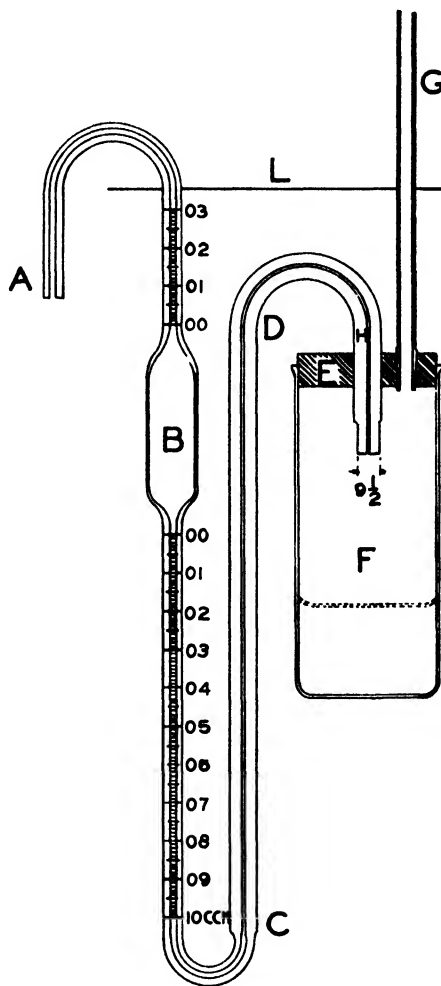


FIG. 17.

Glass Parts of Drop-weight Apparatus for Determinations at a Liquid/Liquid Interface.

Harkins and Humphrey⁵² constructed two types of apparatus for the determination of tension at the liquid/liquid interface. The first apparatus, based on the principle of capillary height, measured the tension of the "dineric interface" by means of a vertical capillary completely immersed in a wide container holding water and on the surface of which is poured, *e.g.*, benzene. By means of a ratchet, the capillary tube

end effect, and as such is not typical of the mechanism of wetting. The wetting tension is a tension with which the contact surface between the solid body and the liquid tends to increase. This tension may be measured by using the principle based on contraction as well as dilatation of a solid surface by wetting; however, this applies only to substances such as rubber. Another principle for measuring the wetting tension is based on the spreading of the liquid on a solid surface by a partial wetting. Thus either the contact angle between the boundaries is measured or the wetting tension is determined directly from the rising height as well as the pressure of the liquid in a capillary.

The wetting tension may be determined from the rising height of an imperfect wetting liquid in a capillary according to the equation:

$$\beta = rhd/2.98/\text{dyne/cm}$$

However, the results are not reproducible by the use of this method.

The method used by Haller⁵⁰ for measuring the wetting tension involves measuring the velocity of displacement of a meniscus in a horizontal capillary at varying pressure. The most important factor is the movement of the meniscus. The wetting tension is obtained from the following equation:

$$\beta = \alpha - \frac{2(h_r - h_s)d}{\delta}$$

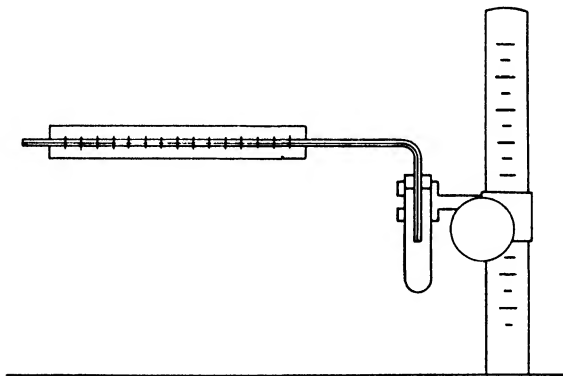


FIG. 20.

where d is the density of the liquid, r the radius of the capillary, h_r the level difference which maintains equilibrium with respect to the wetting tension, and h_s the level difference at which the liquid reverses its flow. In the backward movement of the meniscus, the hysteresis of wetting is so strong that the contact angle is almost always 0° . In the equilibrium state, the wetting tension β is equal to the coherent compound of the surface tension α multiplied by the contact angle δ :

$$\beta = \alpha \cos \delta$$

The velocity of the forward moving meniscus is determined at various pressures, and by extrapolation of zero velocity the pressure, as well as the level difference (h_0), which maintains equilibrium with respect to the wetting tension, is determined.

Capillary-active substances usually form intermediate layers at the solid/liquid boundary and strongly influence wetting. Unstable films do not change the wetting tension, but decrease the wetting velocity. Metastable films decrease the wetting tension. Stable films increase the wetting tension.

The arrangement outlined in Fig. 20 is as follows:

One end of a horizontal glass capillary is bent at right angles and dipped into the liquid to be investigated. The liquid contained in a small beaker may be raised and lowered by means of a rack and pinion. If the level of the liquid is sufficiently high, its height is increased as the

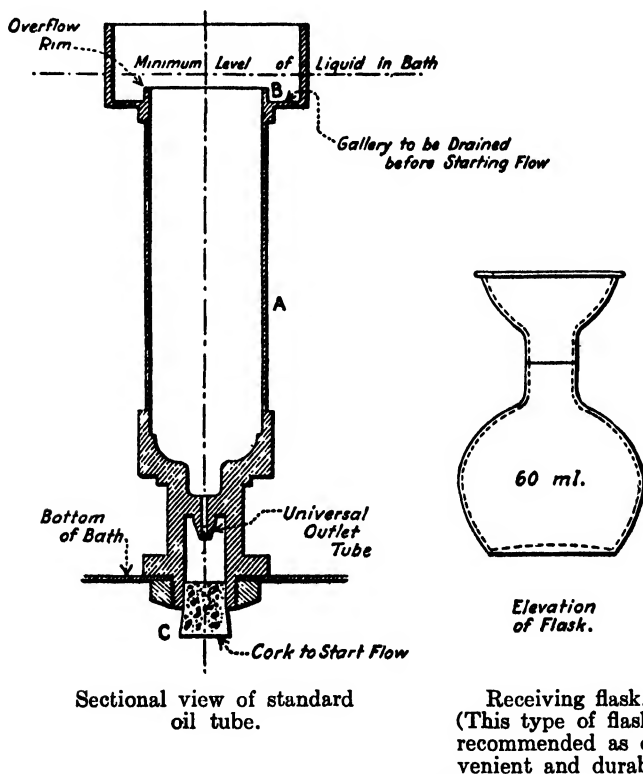


FIG. 21. Saybolt Universal Viscometer.

result of a wetting tension inside the capillary, and moves with a definite velocity in the horizontal position. The velocity with which the liquid moves forward is measured with a mirror scale and a stop-watch. (The height of the outside liquid level is varied). For each measurement a

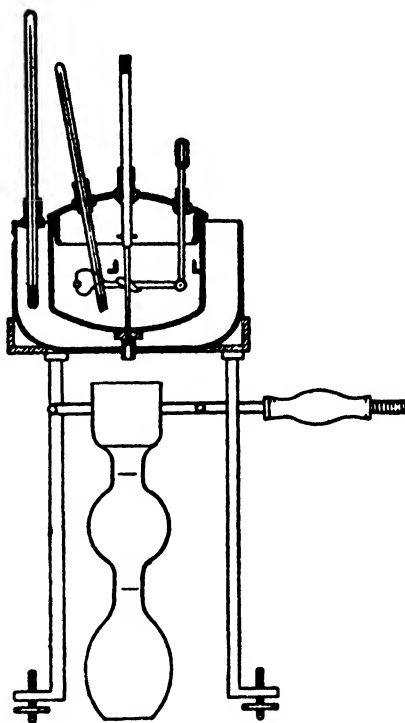
new, dry capillary is used (the length of each capillary must be about the same to facilitate extrapolation). By graphical extrapolation with $V = 0$, the level difference of the liquid is determined for the case when the meniscus does not go forward, as well as that at which it starts to flow again. From this, the difference between the surface tension and the wetting tension is obtained according to the equation:

$$\sigma - \beta = rd/2(hr - hv) .981 \text{ dyne/cm}$$

Viscosity Tests

How important viscosity tests may be is indicated by the fact that the viscosity of a lubricant, or its resistance to flow under anticipated conditions, must be such that a lubricating film is maintained and undue

FIG. 22.
Engler Viscometer.



frictional losses avoided. The viscosity of industrial lubricating oils covers a very wide range. The viscosity of an oil is determined at a definite temperature; the variation in the viscosity of an oil with temperature depends on the character of the oil.

There are three principal types of industrial viscometers for use in testing oils, namely, (1) Redwood, (2) Saybolt-Universal, and (3) Engler. For measuring the viscosity of petroleum products in absolute units with a degree of accuracy greater than 0.5 per cent, five U-tube

viscometers are specified: (1) Ostwald, (2) British Standard Institution (Ubbelohde), (3) Vogel-Ossag, (4) Steiner, and (5) Hoppler.

Redwood, Saybolt-Universal and Engler industrial viscometers are of the short efflux tube type, in which the time of outflow of a definite amount of oil is observed. These instruments consist of an oil cup with an oil-level gauge fitted with a calibrated orifice at the lower end. The oil is maintained at the desired temperature by means of a surrounding bath. The time of efflux for a given temperature is measured and the kinematic viscosity of the oil, proportional to the efflux time, is calculated from the equation:

$$\mu = \frac{\eta}{d} = AT - \frac{B}{t}$$

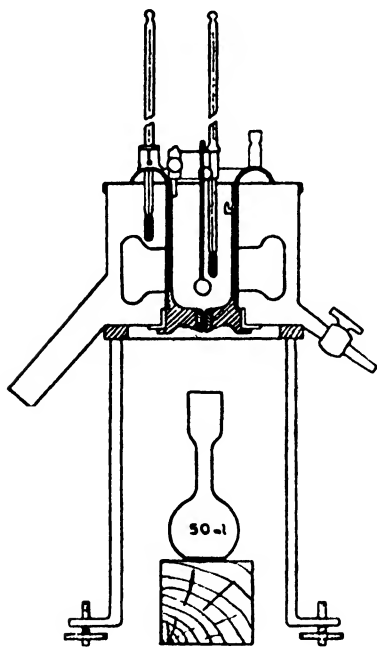


FIG. 23.

Redwood No. 1 Viscometer.

where μ denotes the kinematic viscosity of the oil in centistokes, η the absolute viscosity of the oil in centipoises, d the density of the oil at the same temperature, t time of efflux in seconds, and A and B are constants of the individual instrument. The accuracy of Redwood and Saybolt-Universal viscometers is one per cent; that of Engler, about 3 per cent. The U-tube viscometers are generally of a modified pipette type, constructed of glass, and having long capillary tubes. If the oil flows under gravity, the time of flow is proportional to the kinematic viscosity; but if it flows under an artificially maintained pressure, it is proportional to the absolute viscosity. The U-tube instruments must be calibrated with liquids of known viscosity. The volume of liquid required is materially

less than that necessary for tests in industrial viscometers (Figs. 21, 22, 23).

Measurements of Electrical Properties

Elektrokinetic Potential

A colloidal solution as a whole exhibits no external electric charge, but its particles migrate to a pole in an electric field. This is brought about by the fact that electrically charged particles, when present in an electrically conducting dispersion medium,* are surrounded by an atmosphere of oppositely charged ions. These are equivalent electrically to the adsorbed ions, making the particles as a whole appear to be uncharged. When the particles move, the ionic atmosphere of the

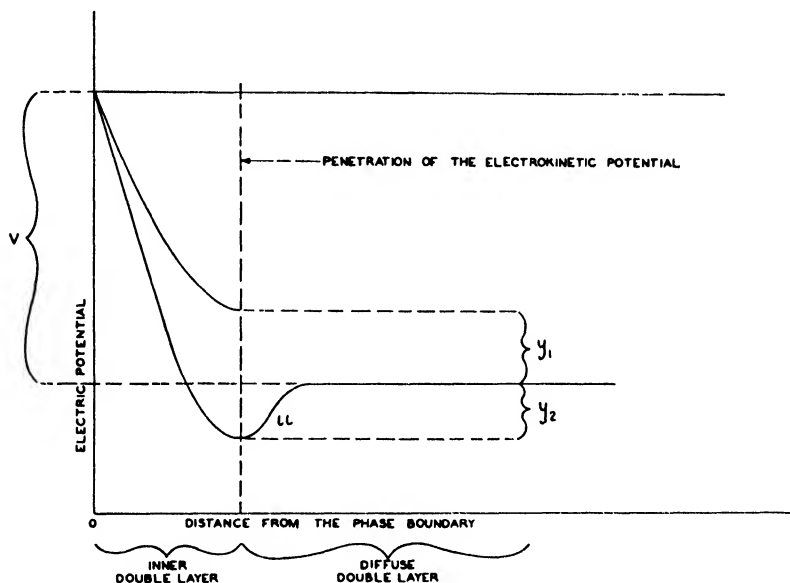


FIG. 24.

particle is sheared and the part adhering directly to the particle is carried along as a result of molecular attraction, there being a potential drop between the particle and the dispersion medium undergoing endosmotic flow.

The boundary layer structure consists in general of two parts, an inner, condenser-like double-layer and an outer or diffuse layer. It is probable that the sheets of the inner layer are separated by but one layer of water molecules possessing a dielectric constant of about 7, the diffuse layer extending into the aqueous phase for a certain distance. The potential gradient, giving rise to the interface potential, is not uniform; in all probability it is steeper over the inner double-layer,

* The phenomena described occur equally well in dispersion media which are not electrically conducting (Abramson) (Görtner).

falling off more gently across the outer or diffuse layer. However, it is possible that a twofold ionic stratification may exist before the outer layer is reached, the potential distance curve presenting a point of inflection as indicated by (ii) in the diagram (Fig. 24). There exists, in addition to the interphase, potential difference V , another potential difference of fundamental importance in the theory of the electric properties of colloids, namely, the electrokinetic potential ζ of Freundlich. Zeta potential is a calculated value based upon certain assumptions for the potential difference between the aqueous bulk phase and some apparently immobile part of the boundary layer at the interface. Thus ζ represents a part of V ; but no method is available for determining how far one must penetrate into the boundary layer before the potential rises to the value of the electrokinetic potential ζ , whether ζ represents part of, all of, or more than the diffuse boundary layer.^{94a}

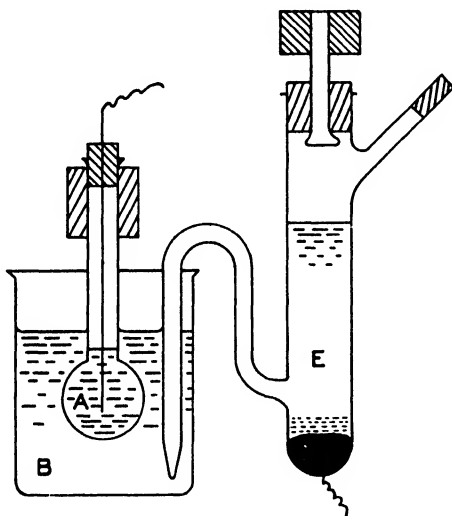


FIG. 25.

The potential difference between the ions adsorbed on the particle and the external dispersion medium constitutes the electrokinetic potential, while the total potential drop from the true particle limit to the internal part of the dispersion medium corresponds to the thermodynamic potential. While ζ potential depends on adsorbed ions, their influence on the change in ϵ potential is insignificant; the concentration of hydrogen ions affects the latter to a great extent. The influence of the nature of electrolytes is significant only when it changes the concentration of the hydrogen ions in one direction or another. The thermodynamic or contact potential (Nernst) may be measured by means of a glass electrode proposed by Haber and Klemensiewicz⁴⁷ which, as shown in Fig. 25, consists of a very thin walled glass bulb (0.06-0.1 mm) containing an electrolyte (potassium chloride solution) in which an electrode connected with a galvanometer is immersed. This electrode is dipped into the solu-

tion contained in a beaker, into which is also immersed the normal electrode E , usually earthed. Depending upon the nature and concentration of the electrolyte in the beaker, for the same liquid contained in the glass electrode, the potential difference between the glass electrode and the electrode in the beaker changes with the concentration of the hydrogen and hydroxyl ions of the solution in the beaker.

In order to characterize a liquid as acid, neutral, or alkaline, it is sufficient to give its hydrogen ion concentration or its hydroxyl ion concentration, as the case may be. The dissociation equation of water is:

$$[H] \cdot [OH'] = K_w, \quad \text{or } h \cdot oh = K_w$$

Usually, the results of measurements obtained are related directly to h and, instead of designating it as the hydrogen ion concentration, it is referred to as "hydrogen number." Sørensen^{109a} introduced the symbol pH, which is $(-\log h)$. The following characterizations for neutral, acid, and alkaline reactions are recognized:

$$\begin{aligned} \text{neutral:} \quad h &= 10^{-7} \\ \text{acid:} \quad h &> 10^{-7} \\ \text{alkaline:} \quad h &< 10^{-7} \end{aligned}$$

For example, in converting h into pH,

$$\begin{aligned} h &= 10^{-7} \\ \log h &= -7, \text{ or} \\ -\log h &= 7 \end{aligned}$$

then

$$\begin{aligned} h &= 2.00 \cdot 10^{-7} \\ \log h &= 0.301^{-7} \\ \text{pH} &= 6.699 \end{aligned}$$

Table 1 lists the hydrogen ion concentration and its equivalent "hydrogen number" of hydrochloric acid and sodium hydroxide solutions.

Table 1
(Sørensen)

	Solution	h	pH
	N Hydrochloric acid	0.80	0.10
0.1	N Hydrochloric acid	0.084	1.076
0.01	N Hydrochloric acid	0.0095	2.022
0.001	N Hydrochloric acid	$9.7 \cdot 10^{-4}$	3.013
0.0001	N Hydrochloric acid	$9.8 \cdot 10^{-4}$	4.009
	N Sodium hydroxide	$9.0 \cdot 10^{-14}$	14.05
0.1	N Sodium hydroxide	$8.6 \cdot 10^{-14}$	13.07
0.01	N Sodium hydroxide	$7.6 \cdot 10^{-13}$	12.12
0.001	N Sodium hydroxide	$7.4 \cdot 10^{-11}$	11.13

In general, at the boundary of two phases a potential difference exists which is based on the peculiar distribution of dissolved electrolytes between phases. It is assumed that each type of ion has its own char-

acteristic distribution coefficient. Thus the coefficients for the positive and negative ion of an electrolyte are not equal. Therefore it follows that the law of distribution does not hold true for the total electrolyte, if it is applicable to its individual ions; and, secondly, that at the boundary a potential difference exists, which stands in a relationship with the electrolytic solution pressures of the single ion type in single phases, thermodynamically calculable. Potential differences may be calculated from the concentration of an ion type common to both phases;

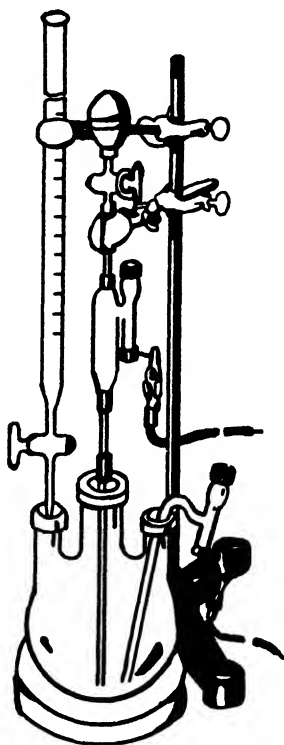


FIG. 26. Hellige Glass Electrode.

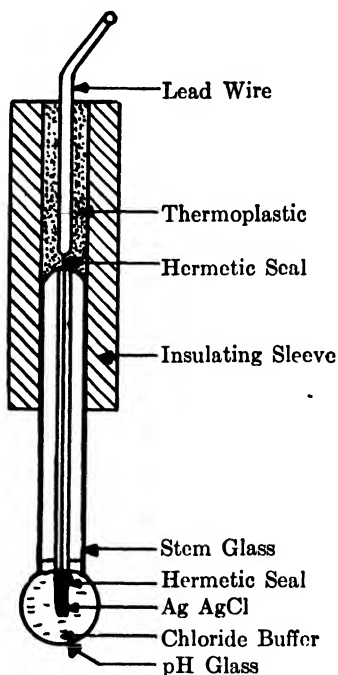


FIG. 27. Coleman Scaled Glass Electrode.

and the electromotive force of the chain formed at one of two boundaries may vary from zero to a definite maximum value, depending on conditions. This value is equal to an ordinary Nernst concentration chain with metal electrodes.

The hydrogen electrode, the quinhydrone electrode, and the antimony electrode are systems which indicate hydrogen ion concentration. The Hellige pH meter, manufactured by Hellige, Inc. of Long Island City, New York, is an instrument suitable for the determination of hydrogen ion concentration with all types of electrode systems. It consists essentially of a direct-reading pH potentiometer, combined with a vacuum-

tube galvanometer as the zero indicator, and measures with ease the glass electrode potential as well as those of other electrodes. Figures 26 and 27 illustrate the two commercially available glass electrodes for measuring pH.

One of the most widely used glass electrodes is the Beckman pH meter manufactured by the National Technical Laboratories, Pasadena, California.

Streaming Potential

To determine the electrokinetic ζ potential, Freundlich and Rona³⁹ devised the streaming potential apparatus (Fig. 28) by means of which the potential generated by flowing a liquid through a capillary, called "streaming potential," is measured. The liquid is forced to flow under

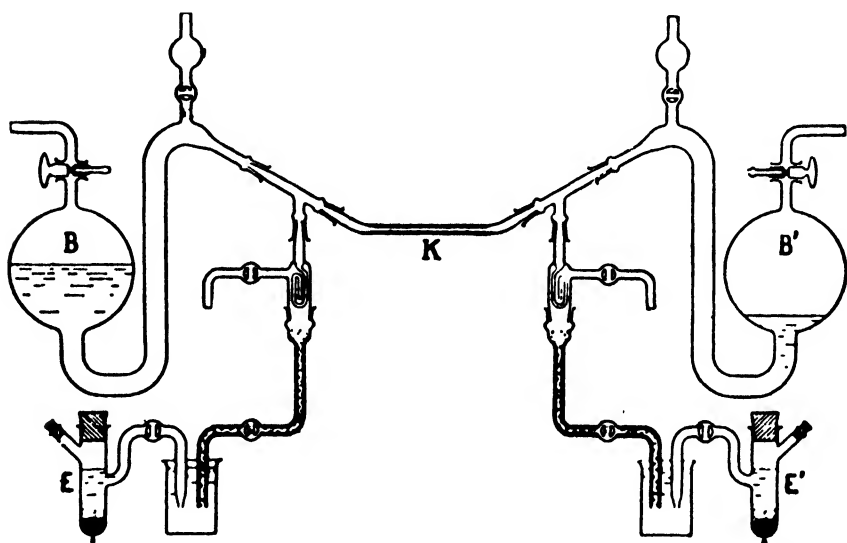


FIG. 28. Freundlich's Apparatus for Measuring Streaming Potential.

pressure from one glass bulb into the other through capillary, K , placed between two electrodes, E and E_1 , and the potential between them is measured. The electrokinetic potential is calculated according to Helmholtz's equation:

$$S = \frac{P\zeta D}{4\pi\eta l}$$

where S is the streaming potential, P the pressure under which the liquid flows, l the distance between the electrodes, η the viscosity of the medium, D the dielectric constant, and ζ the potential of the double-layer. Depending on the conception of the double-layer, the electric double-layer located in the interface may be either immobile (Fig. 29a), or diffuse (Fig. 29b); a selective adsorption of an ion, as well as of colloidal ions

(Fig. 29c), may also take place. If the polar parts do not dissociate, *i.e.*, if polar molecules or dipoles are present, then they accumulate at the boundaries and are oriented (Langmuir, Harkins) and the double-layer is immobile.

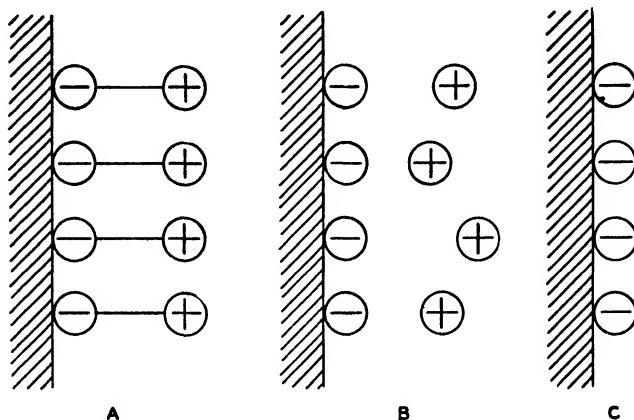


FIG. 29. Structure of the Electric Double Layer

- A. Helmholtz, Smoluchowski
- B. Lamb
- C. Wo. Paul

The theory of the diffuse double-layer given by Stern^{113a} has been discussed by Urban and White.^{118'} Stern's conception of a variable charge governed by adsorption has been found to be sound, and his equation describes the structure of an electric double-layer as being due to ionic adsorption at the phase boundaries; it represents a combination of the Helmholtz and Gouy double-layer concepts. Stern's equation is as follows:

$$\frac{K_0 (\psi_0 - \psi_1)}{\eta} = FZ \left\{ \frac{1}{1 + \frac{1}{18e} e^{\frac{\phi^+ - F\psi_1}{RT}}} - \frac{1}{1 + \frac{1}{18e} e^{\frac{\phi^- + F\psi_1}{RT}}} \right\} \\ + \frac{\sqrt{\frac{DRT}{2\pi}}}{\eta_2} \left\{ e^{\frac{F\psi_1}{2RT}} - e^{\frac{-F\psi_1}{2RT}} \right\}$$

where e is charge of electron; K_0 , capacity of Helmholtz condenser; ψ_0 , potential drop across Stern's double-layer; ψ_1 , potential drop across diffuse double-layer (Gouy) (approximately equal to ζ potential); η_0 , excess negative charges on solid surface; F , 96,500 coulombs; Z , maximum number of mols of ions which can be accommodated in a unimolecular layer of 1 cm² (maximum number of ions = Z); ϕ^- , molar energy

of adsorption of anions; ϕ^+ , molar energy of adsorption of cations; e , concentration of salt in mols per cm^3 ; η_1 , excess positive charges in the Helmholtz layer; η_2 , excess positive charges in diffuse layer; D , dielectric constant; e_a , mobility of anion; e_c , mobility of cation, and η_0 , number of anions in the inner Helmholtz layer, if the cations can be overlooked.

The presence of free charges or separable double-layers in the interface first introduces the possibility of producing a mechanical displacement by tangentially acting electric fields and, in the second place, reveals potential differences by mechanical displacement along the boundaries. The most extensively studied cases are those relating to liquid dispersion media containing solid dispersed particles, whereby the electric field causes either the dispersed part (electrophoresis) or the dispersion medium (electro-osmosis) to migrate. Thus cataphoretic streams are distinguished from streams caused by the migration of the dispersion medium when the dispersed part migrates.

Migration Velocity

The migration of the dispersed component of a colloidal system in an electric field is proportional to its strength, and the direction of the migration is toward either the anode or the cathode. If U is the migration velocity of a single particle under the influence of the strength of the electric field, H ; η , the viscosity; ϵ , the dielectric constant of the medium, and ζ the electrokinetic potential corresponding to the condenser formed by the double-layer, then the equation is expressed as follows:

$$U = \kappa \frac{\zeta H \epsilon}{\eta}$$

where κ is a numerical factor which for cylindrical particles has a value of $\frac{1}{4} \pi$, while for spherical particles it is $\frac{1}{3} \pi$ (Debye and Hückel²⁸).

Bull^{13a} compared the electrophoretic, electro-osmotic, and streaming potential methods of measuring the electrokinetic potential, using the same solution and a protein-coated surface. However, poor correspondence was found between electrophoresis and streaming potential for quartz and cellulose surfaces. Bull obtained the ratio between the zeta potential determined by streaming potential and electrophoresis, by using the following formulas:

$$\zeta_s = \frac{4\pi k H \eta}{DP} \quad (\text{streaming potential})$$

and

$$\zeta_s = \frac{4\pi \eta V}{DX} \quad (\text{electrophoresis})$$

where k is the conductivity in reciprocal ohms, H the streaming potential, η the coefficient of viscosity, P the pressure forcing the liquid through the capillaries, X the potential gradient across the electrophoretic cell,

D the dielectric constant, and V the velocity of the particles. Dividing equation 1 by equation 2,

$$\frac{\zeta_s}{\zeta_o} = \frac{kH}{P} \cdot \frac{X}{V}$$

and introducing the proper constants to convert ordinary units into electrostatic units, the following equation used in calculating the desired values was obtained:

$$\frac{\zeta_s}{\zeta_o} = 7.57 \times 10^3 \frac{Hk}{P} \frac{X}{V}$$

Migration velocity may be measured by means of the Michaelis' apparatus or other cells shown in Fig. 30. For quantitative measurements it is important to use non-polarized electrodes, and an arrangement provided with glass stop-cocks in order that the boundary layer, the migration of which is observed, may be clean.

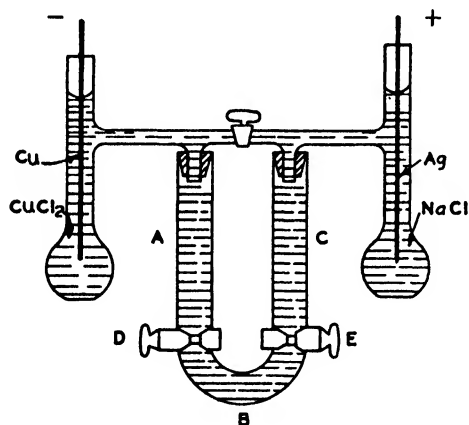


FIG. 30.

Michaelis' Cataphoresis Apparatus.

The ratio of the quantity of electricity transported by the cation and anion depends only on the ratio of their velocities (mobilities). If e_1 is the quantity of electricity transported by the anion; e_2 , the quantity of electricity transported by the cation, and e the total amount of electricity, then we obtain two equations:

$$(1) \quad e_1 + e_2 = e$$

and

$$(2) \quad \frac{e_1}{e_2} = \frac{V}{U}$$

where V and U are the corresponding mobilities of the anion and cation. From this it follows that:

$$(1) \quad \frac{e_1}{e_1 + e_2} = \frac{e_1}{e} = \frac{V}{U + V}$$

and

$$(2) \quad \frac{e_1}{e_1 + e_2} = \frac{e_2}{e} = \frac{U}{U + V}$$

Hittorf, who published the first experiments (1856) on the migration of ions, called $\frac{V}{U + V} = N$ the migration number of the anion, and $\frac{U}{U + V} = 1 - N$ the migration number of the cation. The total quantity of electricity passed through the electrolyte during the experiment is estimated by means of a titration voltameter consisting of a tube provided with a glass stop-cock at the end; through the cork at the top is passed

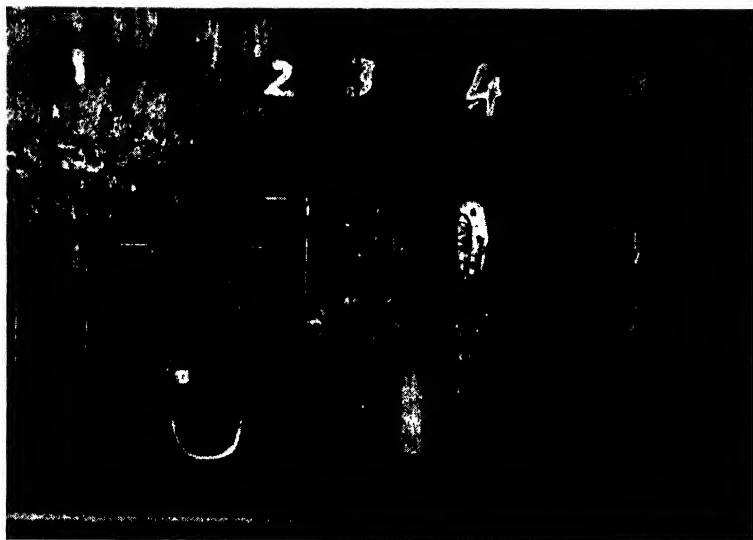


FIG. 30a. Five Types of Cells Used in Studying the Charge on Dispersed Droplets in Oil-field Emulsions. (Abozeid)

a copper wire in a narrow glass tube carrying a silver wire bent upward, which serves as an anode. The cathode is a platinum plate. The tube is filled three-quarters full with a 20-per cent sodium nitrate solution, upon which is carefully poured (to prevent mixing together) dilute nitric acid (1 part nitric acid, sp gr 1.38 per 10 parts water). When the current is passed, the silver anode dissolves. After completion of the experiment, the liquid is poured from the titrating voltameter into an Erlenmeyer flask and the silver nitrate formed is titrated by means of 1/50*N* solution of ammonium thiocyanate. The number of cc used for titration is proportional to the amount of dissolved silver, or to the quantity of electricity passed through the solution during the experiment.

A copper voltameter, the electrodes of which are made of copper

and filled with a copper sulfate solution acidified with sulfuric acid, may be substituted for a titration voltameter. Ettel recommended the use of a solution composed of 150 g of copper sulfate, 500 g of concentrated sulfuric acid, 50 g of alcohol, and 1000 g of water. To prevent oxidation of the separated copper, a stream of hydrogen is passed through the solution.

The cell in which the migration of ions is determined has as its anode a silver wire and as its cathode a copper wire. One arm of the U-tube is filled with a concentrated solution of cupric chloride (3-4 cm), upon which is carefully poured a 1/20N silver nitrate solution (containing 2.125 g of silver nitrate per 250 cm³ of the solution). The same solution fills the other arm of the U-tube, as well as the tube connecting the two arms. To increase resistance, a water rheostat is inserted into the circuit. The equipment for the determination of the migration of ions is illustrated in Fig. 31.

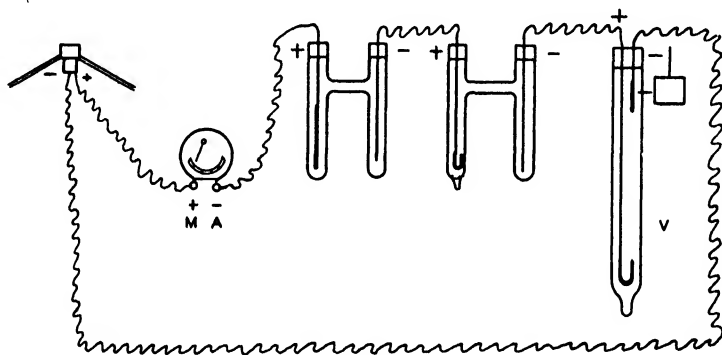


Fig. 31.

Example: Duration of the experiment, 2 hours; current used, 10 mA; titre of the ammonium thiocyanate solution, 12.17 cc, 1/20N silver nitrate corresponding to 40.9 cc of ammonium thiocyanate.

Voltameter: Titration of the liquid indicates 64.0 cc of ammonium thiocyanate. This is proportional to the total quantity of electricity passed through e .

The migration apparatus: 26.01 cc of the anodic liquid is required to titrate 123.7 cc of ammonium thiocyanate. Before the experiment, the anodic solution contained 1/20N solution of silver nitrate. From this may be calculated how many cc of ammonium thiocyanate solution correspond to 26.01 cc of the anodic liquid before the experiment.

$$X = \frac{40.9 \times 26.01}{12.17} = 87.44 \text{ cc NH}_4\text{CNS}$$

Actually 123.7 cc ammonium thiocyanate were used. Therefore the increase in the concentration of the anodic liquid is $123.7 - 87.44 = 36.26$ cc of ammonium thiocyanate. At the anode in the migration apparatus as much silver was dissolved as at the anode of the voltameter. Thus the same increase in the concentration of silver nitrate, i.e., 64.0 cc, should be expected. The difference, $64.0 - 36.26 = 27.74$ cc of ammonium thiocyanate, corresponds to the number of ions of silver carried away by the current, and this number is proportional to the quantity of electricity, e , transported by the cation. From this it may be deduced that 27.74 cc of ammonium thiocyanate is proportional to the amount of electricity, e , while 64.0 cc of

ammonium thiocyanate is proportional to the total amount of electricity used in the experiment, or e .

$$\frac{e_2}{e} = \frac{27.74}{64.0} = 0.433 \text{ (the migration number of silver)}$$

(The migration number of the anion $\text{NO}_3 = \frac{V}{U + V} = n = 1 - 0.433 = 0.567$).

Conductivity Measurements

The electrical conductivity of oils is relatively small; it shows an increase with temperature and plays a special part in testing cable insulating oils. The conductivity test is carried out by means of a cylindrical condenser inserted in a Wheatstone bridge. The outer cylinder containing the insulating liquid to be tested is attached to a source of high voltage and the angle σ , by which the phase angle ϕ of the condenser subjected to a loss deviates from 90° , is measured. The angle of loss, σ , or $tq\sigma$, is then a measure of the electrical property of the insulating liquid.¹⁰⁸

Dielectric Strength Measurements

The question of how to determine the presence of water in oil is important, especially in certain oils. The important factor in transformer oil is its freedom from water. The water content of transformer oil is determined by measuring its dielectric strength. Descriptions of commercially available tests for transformer oils are given in Westinghouse and General Electric bulletins.

Schröter found that impurities present in oil formed bridges between electrodes, causing breakdown when voltage is applied, all the particles with dielectric constants higher than the oil moving into the field. The high dielectric constant of the filament path through the oil has been found to be a function of its water content. With increasing water con-

Table 2.

(Stark ¹¹³)

Water in Oil (Volume %)	Break-down Voltage (KV)
0.005	31
0.01	22
0.02	16
0.03	14
0.04	13
0.05	12.5
0.10	10

tent the strength of the oil decreases, at first rapidly and then more slowly, tending to reach a limit at about 20 kv/cm. As the principal insulating material is oil used in high-voltage transformers and switches, it is important that it be cleaned carefully and dehydrated. The content of water in a transformer oil as shown by Schröter's observations, may be determined by measuring the dielectric constant.¹⁰² If water is

present in transformer or switch oils, a loss occurs in dielectric strength, which is an important factor in an insulating medium. The following figures give an estimate of the extent to which water reduces the dielectric strength of a mineral transformer oil.

These tests were carried out on a disc electrode machine (diameter of disc, 0.5 in; distance between discs, 0.2 in). Brass disc electrodes one inch in diameter with flat parallel faces spaced 0.1 in apart are used in standard tests.

The dielectric constants of petroleum products vary from 1.8 to 2.6, as indicated in Table 3. The dielectric constant of air is only 0.0006 greater than the value for vacuum.

Table 3. Dielectric Constants of Petroleum Products

Product	Dielectric Constant
Gasoline	1.85-2.0
Kerosene	2.0 -2.2
Transformer oil	2.1 -2.3
Lubricating oil	2.1 -2.6
Vaseline	2.05-2.3
Paraffin liquids	2.05-2.1
Crude oils (Roberts)	2.2 -3.6

The dielectric constant ϵ of a material is defined as the ratio of the capacity of a condenser with a substance between the condenser plates, C , to that of an empty condenser under vacuum, C_0 or $\epsilon = C/C_0$. Therefore, in order to measure the dielectric constant, it is necessary to compare the capacity of suitable condensers (or measuring cells for liquids), both filled and empty, with that of a standard condenser, using an appropriate measuring circuit. Alternating-current bridges for frequencies up to 50,000 cycles, as well as resonance circuits or heterodyne beat methods for the higher radio frequencies may be used as measuring circuits. Measuring cells for liquids consist of a cup-shaped electrode surrounding another electrode, and may be either concentric cylinders or parallel plates. To eliminate edge effects and stray capacities, a third ("guard") electrode is often used. Dielectric constant data give a measure of the amount of undesirable materials in petroleum products and indicate the oxidation of petroleum products. According to Debye's theory, materials composed of non-polar molecules have dielectric constants essentially equal to the squares of the refractive indices (the optical dielectric constants), whereas materials containing polar molecules have dielectric constants which are greater than the squares of the refractive indices. Highly refined petroleum products are made up almost entirely of saturated hydrocarbons, which are non-polar materials. The unsaturated hydrocarbons are usually weakly polar, while resins, asphalts and all oxidized hydrocarbons are polar. Thus crude oils and semi-refined and deteriorated petroleum products, being mixtures of weakly polar and non-polar substances, have dielectric constants approximating the order of polar materials. The refining of petroleum makes the dielectric constant nearly that of non-polar materials.

Since the dielectric constant of oils almost always decreases with increase in temperature, some form of temperature control in measuring dielectric constants should be provided.

When mineral oils are heated while exposed to air, oxidized compounds, such as peroxides, alcohols, acids, and esters, are formed. These are polar in nature, and the formation of polar molecules causes an increase in the dielectric constant of the oils, which increases with time of ageing. Stoops¹¹⁴ used the increase in the dielectric constant as a measure for the oxidation of oils. In addition, it has been found in the case of oxidation of oil that the formation of polar compounds not only caused an increase in the dielectric constant, but also increased the spreading of oil films on water. A partial ionic dissociation of polar compounds causes an increase in electrical conductivity. Thus measurement of changes in various electrical properties of oils in general, as well as in emulsified oils, is important because the data obtained may be used in judging their suitability for certain purposes.

Measurements of changes in the electrical properties of oils with artificial ageing have been used in studying the stability of transformer oils and oils for use in high-voltage cables.

Paraffined and oil-impregnated paper condensers, and insulated oil-impregnated paper cables are types of electrical equipment in which dielectric constants of petroleum products used are of importance. The dielectric constants of the hydrocarbon-cellulose combination are about 4.¹⁰⁹

In oil-impregnated paper cables, from the power-consumption standpoint, it is desirable that the dielectric constant be as low as possible; but from the standpoint of stability of the insulation under high voltage, it is desirable to have a higher dielectric constant for the impregnating material. In the case of paper-insulated cables, impregnating materials of higher dielectric constant are preferred.^{97a}

Tensile Strength Test

Oil in general, and pure linseed oil in particular, is the best liquid binder known for cores. Because of the prohibitive cost of pure linseed oil, it is often replaced in part (10-15 per cent) by a neutral mineral oil. Neutral mineral oil has practically no binding power, while drying oils are essential as binding agents in a core-oil blend. Fish and whale oils are good binders, but give off disagreeable odors.

The finding of an efficient and economical oil as a core binder is important in foundry practice; it also aids in determining the strength of cores. Cores are shaped in molds, usually of wood construction, one inch wide and 15 inches long with a 1½-inch clearance at either end for support. (When using an oil of low binding power, the length of the bar should not exceed 6 inches). A method of determining the strength of a core is as follows: A bucket supported on a wire is hung from a core and shot is poured into it until the core breaks. From this the weight required to break the core is determined. However, this method is crude

at best and is not sufficiently sensitive for cores with low "breaks"; therefore resistance to rupture or tensile strength is determined. Usually, it is necessary to determine the relative strength of two cores in order to compare the value of two core binders.

Emulsification and Demulsification

Obviously, devising a satisfactory test method for the determination of the quality of an oil with regard to its freedom from emulsion-forming tendencies is of great importance. Various attempts have been made in this direction, but little success has been achieved. The U. S. Bureau of Standards has worked out a test that shows the rate at which equal quantities of oil and water will separate when mixed together under certain conditions, and the term "demulsibility" has been proposed for the property so indicated. But the rate at which two oils may separate from water is not an indication of the completeness of the separation. An oil separating rapidly from water may leave a thick layer of emulsion between the water and oil at the end of the test. Another oil, separating more slowly, may leave no such layer of emulsified oil.

Demulsibility is defined by Herschel as the maximum rate of settling out of an oil from a prepared emulsion expressed in cubic centimeters per hour, and is determined as follows: 20 cc of oil and 40 cc of distilled water are placed in a 100-cc flask (inside diameter, 26 mm), heated on a water bath to 55°, and the mixture stirred with a metal paddle $\frac{1}{8}$ inch wide and $3\frac{1}{2}$ inches long for 5 minutes at a speed of 1500 r.p.m. The average rate of settling between the time stirring has ceased and observations are made is calculated from the readings of the amount of oil settled out from the emulsion.*

Demulsibility is also a measure of the resistance of an oil to emulsification; therefore demulsibility has been taken as the number of cubic centimeters of oil which have settled out in an hour.

Oils which show no signs of settling out at the end of one hour are said to have zero demulsibility. For this test the Herschel emulsifier designed by C. W. Stratford for the Tidewater Oil Company and the emulsion testing machine in use at the United States Naval Experimental Station at Annapolis, Maryland, have been recommended.

Lederer,⁶⁸ from his work on demulsification, developed the following formula:

$$\frac{dV}{dt} = K(1 - V)V^{1/2}$$

where t denotes time, V the volume separated from the emulsion, and K the velocity constant. He also applied the half-time value of demulsification deduced from this formula to characterize demulsification processes and the action of emulsifiers. The constant for the "lower"

* Test method outlined by the Committee on Standardization of Petroleum Specifications, April, 1920.

demulsification limit (separation of water) is about twice as great as that of the "upper" demulsification limit (separation of oil), although considerable deviations exist for this rule.

On the other hand, a method of measuring the ability of oils to emulsify with water should be of great importance in determining the character of an oil. Pick⁸⁸ proposed a method for measuring the emulsifying tendency of fats. A commercial alternating current of 120 volts is conducted through a 50-candlepower electric lamp to copper electrodes placed parallel to each other and plunged into the emulsion. The time noted is from the instant of immersion of the electrodes until the light begins to glow, and is the measure of the stability of the emulsion. Pick measured various fat-water emulsions, such as lecithin mixtures and whale and margarine oil of especially good emulsifiability. For more stable emulsions, 200 volts serve to better advantage.

The shape and size of the electrode and the disposition and length of the gap should be considered, because it is voltage gradient and configuration of the electric field, rather than applied voltage, which are important. In connection with this test method, it may be pointed out that it is by no means infallible, since it depends not only on the emulsifying ability of the oil, but also on its susceptibility to electrical dehydration.

The American Society for Testing Materials developed a standard method (D157-27T) for determining the emulsifiability of lubricating oils.* In practice a simple test is used to determine whether the oil emulsifies readily or not. It consists in filling a four-ounce bottle with equal parts of water and oil; it is shaken vigorously for one minute and then allowed to settle. In this way the rate and degree of separation are determined. The temperature of the water and oil must be the same in comparable experiments.

Herschel⁸⁶ describes a test of emulsification according to which the oil to be tested is placed with double its volume of water in a graduated glass cylinder. A flat metal paddle carried on a vertical shaft is electrically rotated; the speed is indicated by a tachometer attached to the upper end of the shaft, and the rate of speed obtained by means of a rheostat. The relation between speed of agitation (revolutions per minute) and stability (in terms of the number of cubic centimeters of clear oil rising to the top of the emulsion per hour) is recorded. In Conradson's test method,²² steam is introduced into a calibrated beaker containing 200 cc of water and 100 cc of oil for 15 minutes and kept for one hour in water at 130° F. The amount of clear or turbid oil over the emulsion indicates the emulsifiability of the oil.

Morris⁸⁰ described an apparatus used to determine whether or not emulsification may occur within the oil sand. A pipe chamber 6 inches in diameter and one foot long is tightly rammed with sand ranging in grain size from 30 to 40 mesh and having a porosity of about 34 per cent.

* New and Revised Tag Manual for Inspectors of Petroleum, pp. 108-111.

The crude petroleum and water are forced under controlled pressure through the sand column, the outlet from the sand container being through a slotted metal plate. The oil examined was 21.8 Bé San Joaquin Valley California crude, with a viscosity of 933 seconds Saybolt at 68° F. The oil was saturated with dissolved gas at the pressure used in forcing it through the sand. Flow velocities were measured, and ranged from 0.0087 to 0.0495 cc per second under 30 to 62 pounds pressure.

Femme³³ describes specific tests for asphalt emulsions: (1) Wash test to show the cementing time: 1000 g of gravel dried at 105° are dipped for 2 minutes into an emulsion and allowed to drain for 30 minutes. The gravel is then washed with distilled water and dried. The treated and untreated gravel samples are compared. The test is designed to show the degree of demulsibility of asphalt emulsions on gravel. Emulsions which break quickly give 80 to 100 per cent and those slowly separating 2 to 40 per cent of asphalt residue. (2) A demulsification test: 100 g of the emulsion are mixed for 2 minutes with 35 cc of 0.02N

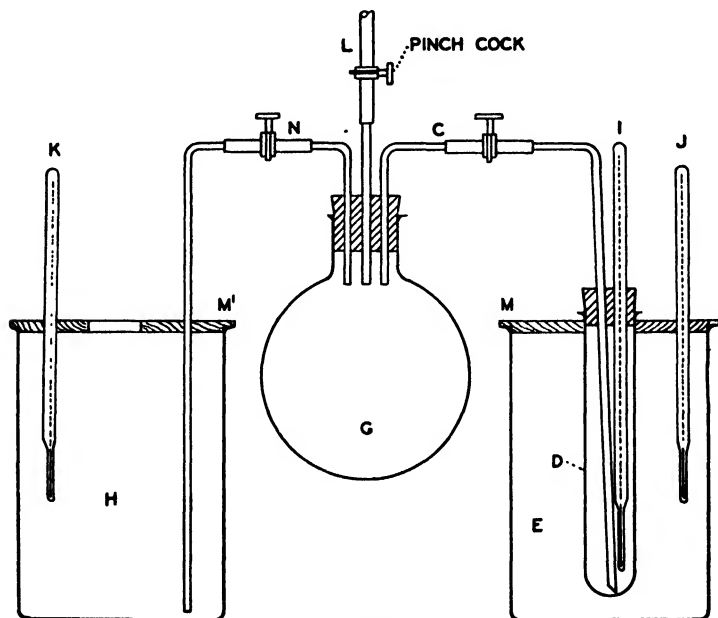


FIG. 32.

calcium chloride solution and the separated asphalt is weighed after washing and drying. (3) A test for determining settling or stratification: Two average samples of about 50 cc are pipetted from the surface of the emulsion, 400 cc from the middle, and 50 cc from the bottom, and the amount of residue after distillation is determined. The difference between the asphalt content of the surface and at the bottom must not be higher than 6 per cent.

The demulsification apparatus in Fig. 32 is used in the modified Conradson steam-blowing test devised to determine the rapidity of separation of an emulsion of oil and water. A steam generator is arranged to blow dry steam through a sample of the oil contained in a graduated tube surrounded by a water bath at 70° F. Steam is passed so that the oil is maintained at 190° F, or until its volume increased from 20 to 40 ml. The tube is then transferred to a separating bath at 200° F and the time of separation of 20 ml of oil is observed (to a maximum of 20 min). The time required is the steam emulsion number in seconds ASTM, and the demulsification number in minutes IPT. For steam-turbine lubricating oils the demulsification test is the most important specification next to viscosity.

Investigation of the Emulsifier

As a rule, so-called emulsifying agents are present in all kinds of emulsions having an appreciable degree of stability. Therefore, it is necessary to determine the nature and function of the emulsifiers as active agents in the formation of emulsions in crude petroleum. In this connection, the importance of studying naphthenic acids or their soaps as emulsifiers has been recognized. One series of hypotheses assumes that naphthenic acids are formed simultaneously with the hydrocarbons of the crude oil and that the unsaturated acids are formed from fats. If this organic genesis theory holds true, saturated fatty acids should accompany naphthenic acids in petroleum (Engler). Another series of hypotheses considers naphthenic acids as secondary conversion products of hydrocarbons. Air oxidation of petroleum leads to the formation of small amounts of naphthenic acids (Mendeleef, Hahn,⁴⁸ Cloez²¹).

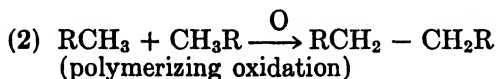
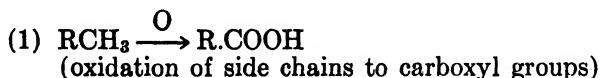
Braun¹² states that naphthenic acids contained in almost all kinds of petroleum have the constitution described by the formula $C_nH_{2n-2}O_2$, or $C_nH_{2n}COOH$, and are considered to be derivatives of cyclohexane or probably cyclopentamethylene having an open alkyl side chain on the ring and a carboxyl group in the molecule. The position of the carboxyl group is assumed to be in the polymethylene ring itself. Braun worked out a method to determine whether the CH_2CH group or $\equiv C$ may be found near the carboxyl group in the acid. The method consisted in allowing phosphorus pentachloride to act upon a monoalkyl amide of carboxy-acids ($R.CONHR'$) in order to decide whether in its acid the group $-CH_2 > CH$ or $> C$ is present in the neighborhood of the carboxyl group. When this method was applied to naphthenic acids of various origins and molecular weights, the surprising result obtained indicated that in them the grouping CH_2CO_2H is predominant, i.e., that the seat of the carboxyl group was not the polymethylene nucleus, but rather that it was bound to the alkyl side chain. This fact led to an investigation of the disintegration of naphthenic acids, similar to that for paraffinic carboxy-acids, and gave an insight into their structure.

Braun investigated a naphthenic acid of the formula $C_{10}H_{18}O_2$ or $C_9H_{17}COOH$, an intermediate molecular size present in Roumanian petroleum. He transformed it to the amide, $C_9H_{17}CONH_2$, decomposed it to an amine, $C_9H_{17}NH_2$, split off a benzoyl compound with phosphorus bromide to form benzonitrile and the bromide, $C_9H_{17}Br$, and finally obtained an alcohol, $C_9H_{17}OH$, by hydrolysis. However, because the properties of the various naphthenic acids in petroleum are so widely different, the question of their structure is still open.

The fact that petroleum treated with sulfuric acid is not essentially richer in low-boiling hydrocarbons as compared with crude petroleum is explained by Zaloziecki^{127a} as due to the formation of dark-colored oxidation products and of water, which dilutes the acid and precipitates from it some of the dark, oil-soluble products of the refining process. The relation of the color of the product to oxidation during acid treatment was confirmed by Condrea, who found that mechanical stirring during treatment gave a light-colored product and that air and oxygen agitation yielded successively darker oils.

Zaloziecki^{127b} noted the formation of fatty acids of low molecular weight by the oxidation of mineral oils. This tendency to form low molecular acids, together with the formation of complex substances which are probably lactones or anhydrides, has hindered the technical production of organic acids by the oxidation of petroleum oils. The most serious difficulty lies in the lack of chemical homogeneity of the oils used as starting materials.^{42a}

Of greatest importance in the oxidation of naphthenes to naphthenic acids, as studied by Charitschkoff,^{18d} are the oxidation of side chains to carboxyl groups and the polymerization by oxidation as expressed in reactions (1) and (2)



Formation of fatty acids from paraffin wax involves chiefly the oxidation of side chains, as in: $\text{RCH}_2 - \text{CH}_2\text{R} \xrightarrow{\text{O}} \text{RCH} = \text{CHR}$, and the breaking of chains at double bonds already formed by oxidation as in: $\text{RCH} = \text{CHR} \xrightarrow{\text{O}} \text{R.COOH} + \text{R.COOH}$.

The oxidation of residue to asphalt involves, in all probability, polymerizing oxidation, unsaturating oxidation, and ring-closure oxidation, together with oxidation of side chains, followed by dehydration and degradation of the carboxyl compounds formed.

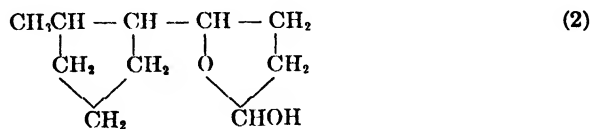
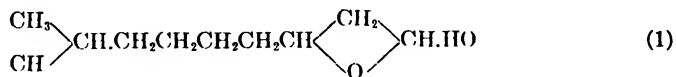
Charitschkoff^{18a} supported the idea that lubricants are saturated cyclic hydrocarbons resembling naphthenes and polynaphthenes.

By determining the physical properties of carefully separated fractions of petroleum oils, it is sometimes possible to calculate the percentage of paraffins and naphthenes, if the corresponding properties of the paraffin and naphthene hydrocarbons are known. Markownikow^{73a} and Engler-Höfer^{32a} therefore applied specific gravity, refractive index, and the specific refractivity of Lorentz and Lorenz, $\frac{N^2 - 1}{(N^2 + 2)d}$, for interpolation. Most of the work on naphthenes has been confined to the monocyclic hydrocarbons. It is quite probable that compounds built up of two or more rings, which may or may not carry side chains, are present in the higher-boiling petroleum fractions, even in paraffin wax. Such compounds would be saturated, but of the composition C_nH_{2n-2} , C_nH_{2n-4} , *et al.*, depending on whether two or more cycles are present; the rings may be joined by one, two, or more common carbon atoms, as in the case of aromatic compounds.

Charitschkoff^{18c} studied the production of naphthenic acids by oxidation of naphthenes. A considerable amount of polynaphthenic acids is produced in this way.

Naphthenic acids possess distinct acid properties, forming stable salts with many metal oxides. On the other hand, the same acids have the properties of anhydrides and alcohols. For example, they give the Rosenthal's reaction¹⁸ with hydrochloric acid and vanillin; the chlor-anhydrides obtained show certain specific properties, such as difficult decomposition by water and alkali, and after decomposition present the appearance of compounds of unknown composition, in addition to the acids. These compounds have an aromatic odor similar to simple ethers. Zalizetsky assumed that the ability to replace the hydroxyl group with iodine by the action of halides in the presence of phosphorus proves the alcoholic properties of naphthenic acids.

Hell and Midinger (1874), and also Brune,¹²⁵ considered naphthenic acids to be lacto-alcohols. Zalizetsky and Brune¹²⁸ proposed two formulas for decanaphthenic acid:



Both formulas explain the Rosenthal's reaction, but do not explain the acid function of the alcohol group.

When naphthenic acids are treated with sodium hydroxide in the presence of a neutral oil, not only the acids, but the neutral oils partially emulsify and partially go into solution. The emulsified portion usually

decreases with an increase in the concentration of the alkali, as stated by Gurwitsch,⁴⁶ in the case of gas oils. The amount dissolved increases when the alkali concentration reaches 2 to 2.5 per cent. Naphthenic soaps, acting as emulsifiers, may be decomposed by means of sulfur dioxide so that a part of the soap is removed, together with the precipitated acids, and hydrolysis is avoided. The sodium acid sulfite or the sodium sulfite is regenerated by means of caustic lime. When naphthenic acids are treated with sulfur dioxide, the emulsion separates into layers, and the resinous substances accumulate in the acid layer. Usually a large excess of sulfur dioxide is necessary, or separation of the naphthenic acids will be incomplete (about 40 per cent of naphthenic acids remain undecomposed).

Rakusin⁹³ describes a method by which he determined the content of naphthenic acids in petroleum. He used a petroleum emulsion from Grozny which was acidified and shaken with ether. The residue was a slightly colored oil, insoluble in water, but which dissolved in an aqueous caustic soda solution with liberation of carbon dioxide. A thick, colorless, non-crystallizing oil was obtained. After evaporation on a water bath and treatment of the remaining soap with 95-per cent alcohol, the naphthenic acid was precipitated. The content of naphthenic acid, for that particular Grozny petroleum, was found to be 1.3820 g per liter. Of course, different soaps behave differently. The barium salt is a white voluminous precipitate, soluble in boiling water; the lead salt, a white precipitate, soluble in hot water; the copper salt, a green precipitate; and the silver salt, a white, cheeselike precipitate, partially soluble in boiling water.

According to Kolbe,⁶⁷ sodium naphthenates are used as emulsifiers because of their good foaming ability.

For determining the nature and properties of the emulsifier present in an emulsion, mention may be made of Pyhala's tests.⁹² In these tests he describes the determination of the emulsifier in a Tschelkener (Russian) crude-oil emulsion containing 20 per cent of water. About 100 g of the emulsion was diluted with 400 cc of benzene and allowed to stand for 24 hours. The clear benzene layer was drawn off with a pipette. The brown aqueous layer containing a jelly-like, creamy precipitate was shaken with 160 cc of a 1:1 ether-alcohol mixture. A light, yellow flocculent precipitate appeared immediately and was filtered off, dried, transferred to a dish by means of hot benzene and evaporated on a water bath. About 0.34 per cent of ozokerite was obtained. The filtrate was weighed and salted out with hot water. The emulsion contained 2.9 per cent of salts and 0.1 per cent of lime and sand. The emulsion examined was a paraffin crude stabilized by precipitated ozokerite. The ozokerite, together with sand, is held in suspension by water containing a considerable amount of salt.

Dow^{30a} stated that results obtained in the laboratory indicate ordinarily that when an oil is cut and the emulsion stratifies the oil in the emulsion, it contains a higher percentage of asphalt than the original

oil.* It is believed that asphalt in crude petroleum is present as a colloid, and that in the process of emulsification in the well it acts as an emulsifier and forms a film around each droplet of water. Thus, according to Dow, when this emulsion is collected and resolved, the oil obtained from it contains the asphalt from the films in addition to the original asphalt. To determine the action of asphalt as an emulsifying agent, a sample of black Bristow (Oklahoma) crude was filtered through fuller's earth and the filtered oil agitated with distilled water. No emulsion was produced even after one hour of agitation. However, Roberts reports that emulsification still takes place.

Two tests have been recommended for the determination of asphalt: (1) The carbon-residue test[†] which involves heating a weighed sample of residuum of the oil from the emulsion in a porcelain crucible placed in turn in a Skidmore crucible. These two crucibles are then placed in a large iron crucible and both are covered. Heating is continued while the volatile substances of the oil are coming off; it is then increased and held high for five minutes. The porcelain crucible is removed, cooled, and weighed. In this manner the difference between the percentage of carbon residue contained in the oil from the emulsion and the original oil is obtained, and it corresponds to the asphalt content. (2) A small quantity of the residuum from the distillation is mixed with sand in order to spread the oil in a thin layer on the grains of sand. The sand is then poured into a cellulose thimble and placed in a Soxhlet extractor. Acetone is used for extraction because it is a solvent for oil and wax, but not for asphalt. When no more oil remains in the sand, the acetone is removed and benzene, a solvent for asphalt, is substituted. The benzene-asphalt solution is evaporated, and a hard brittle asphalt, representing the asphalt content of the residuum, is obtained.

Investigation of the Demulsifier

Tests for demulsifying agents are as follows: (1) Test used in selecting the demulsifying agent most suitable for the emulsion in question. (2) Tests defining qualitative and quantitative composition of the demulsifier. (3) Tests determining the suitability of the demulsifier for electric dehydration.

The most effective demulsifier is selected by pouring uniform 100-ml samples of an emulsion into bottles and adding, by means of a wooden stick or a glass rod, a drop of each of the agents. The mixture is shaken for several minutes, the bottles allowed to stand at atmospheric temperature, and the tendency to break estimated. Sometimes heat is employed. Only those demulsifying agents which show complete break of the emulsion at atmospheric temperature are considered. This test is repeated with the most favorable demulsifiers, but in the form of

*Dow's statement should by no means be considered as always holding true, because concentrated stable emulsions occur in crude oils which contain no asphalt, for example, Gulf Coast, Grade "A," oil (Roberts).

[†] Technical Paper 323A, U. S. Bureau of Mines, 89 pp. (1924).

solutions or dispersions of definite concentration (5 or 10 per cent), added by means of a pipette. If heat is applied, it must correspond to a temperature at which field installations are expected to operate, that is, 120° F. The object of the test is to find the compound which, in the lowest concentration, gives the best and most complete demulsification.^{41a}

Tests of the composition of the demulsifying agent are important only for those interested in the manufacture of demulsifying agents.

Tests conducted with reference to the use of chemical demulsifying agents in conjunction with other dehydration processes, especially electric dehydration, involve the use of a miniature dehydrator, holding about a one-liter sample of the emulsion and operating under temperature conditions corresponding to those under which the dehydrator actually functions on a large scale.^{41a}

Stability

Closely related to the emulsification test is the test for determining the degree of stability of emulsions.¹²⁴ The emulsion to be examined is heated in an autoclave for one, two, and finally three hours, using various pressures. First the emulsion samples are heated for one hour under one atmosphere pressure, the autoclave opened and the emulsion examined. If it is not decomposed, a second test is made with a fresh sample. This time the emulsion is heated for one hour, but under two atmospheres' pressure, and heating continues until conditions are reached under which the emulsion is resolved. By expressing time as the numerator and pressure as the denominator of fractions (1 atmosphere and 1 hour = 1/1), Wischetravsky introduced for 1/1 the term of 1 degree stability. As indicated in Table 4, degrees of emulsion stability may be differentiated by varying the time and pressure factors.

Table 4
(Wischetravsky)

Atm	Hours	Degree of Emulsion Stability
1	1	1
1	2	2
1	3	3
2	1	4
2	2	5
2	3	6
3	1	7
3	2	8
3	3	9
4	1	10
4	2	11
4	3	12
5	1	13
5	2	14
5	3	15
6	1	16
6	2	17
6	3	18

It is of interest to note that Wischetravsky found cases of American emulsions in which breaking could be brought about only at six atmospheres, whereas the Grozny (Russian) type could not withstand more than three atmospheres and one hour of heating.

Putochkowski and Strukowa⁹¹ claimed that centrifuging is a more rapid method of determining stability.

Instability of emulsions may be ascribed to changes occurring in the protective film, which may become brittle and eventually crack, thus leading to a separation of the emulsified phase. The break in emulsions stabilized with soaps, on prolonged standing, has been observed by McBain and attributed to the gradual transformation of the dense soap film at the interface into curds. On the other hand, Nugent^{83a} observed that caustic soda broke a benzene-water emulsion stabilized with gelatin (caustic soda strips the film layer by layer), and that the breaking was preceded by an inhibition period which increased with the age of the emulsion. From this Nugent assumed that the gelatin film increased in thickness with age, the inhibition period being a measure of the thickness of the gelatin layer. Thus, in some cases, the protective film appears to become more resistant with age and the apparent stability of the emulsion increases, not decreases, on standing.

The ageing of the interface between aqueous solutions of sodium oleate, sodium stearate, and mineral oil was studied by Andreas, Hauser, and Tucker.^{2a} They used the method of pendant drops, considering it particularly suitable because of instantaneous determinations of interfacial tension at any desired time interval without disturbing the surface under observation; boundary tensions were found either to increase or decrease during the ageing of an interface.

Determination of Emulsion Type

It is not always easy to determine which of the phases is the continuous one. The test may be carried out by means of electrical conductivity measurements. The conductivity is much higher when water containing small proportions of electrolytes is the external phase. Water-in-oil emulsions with oil (an electrical insulator) as the continuous phase will not conduct electricity. This idea was proposed by Clayton¹⁹ and later used by Sherrick¹⁰⁷ and Bhatnagar.⁹

Bhatnagar's test consists in examining emulsions in a container provided with two platinum electrodes at a fixed distance. A current is applied for 1-2 seconds. With emulsions of the oil-in-water type, 10-13 milliamperes may be used; for the opposite type a very small current of the order of 0.1 milliampere is passed through.

The drop-dilution method for determining the type of emulsion is based on the principle that an emulsion may be diluted by adding the continuous phase, but not by adding the disperse phase. Pickering⁸⁹ has shown that 99 per cent by volume of mineral oil in a one-per cent soap solution may be diluted with water, but does not mix with paraffin

oil. The test is carried out by placing a drop of an emulsion in a small amount of water and stirring. If the emulsified globules diffuse in the water, then water is the external phase; otherwise water is the internal phase.¹³ Hall⁴⁹ modified the test for emulsions which are not too opaque and dark in color. A drop of one of the liquids making up the emulsion is placed in the emulsion near the glass wall of the container. If it is the continuous phase, it diffuses rapidly into the surroundings, forming a less opaque area; if it is the disperse phase, it moves through the emulsion. In water-in-oil emulsions Hall observed that water sinks as a clear drop, whereas oil rises and diffuses.

Woodman¹²⁶ found the drop-dilution test unsatisfactory when dual emulsions are formed, and recommended that the test be carried out both in the water and in the oil phase, using aged emulsions.

The indicator method is described and used by Robertson,⁹⁷ and also by Newman.⁸² A dyestuff, for example Sudan III, a red dye, soluble either in one phase or the other, is dusted on the surface of the emulsion to be examined. If the oil phase is the continuous one, Sudan III, oil-soluble and water-insoluble, will spread throughout the oil; if water is the continuous phase, no spreading of the dye will take place; instead it agglomerates at the oil globules with which it makes immediate contact. Iodine and methyl orange are employed as indicators in testing the phases of benzene-water emulsions. Iodine is soluble in benzene, and methyl orange is soluble in water. Nile blue and scarlet red are used by Hall⁴⁹ as indicators for emulsions of water in various organic liquids. According to Joshi,⁹⁶ the great differences in surface tension and viscosity between oil-in-water and water-in-oil emulsions can be applied as indicators of the emulsion type.

Determination of Emulsion Constituents;

Acidity Test and Salt Tests

Salt and Acid

Salt and acid determinations in petroleum are important. In the analysis of crude-oil systems, the nature of the salt content is first determined and then specific determinations of salts corrosive to refinery equipment made. The determination of free acids (strong and weak) is of considerable importance, as well as the potential acidity. The source of the acidity of aqueous extracts may be found in the processing connected with production methods (acidizing wells with hydrochloric acid which leaves the residual brine particles in the oil highly acidic) and in the demulsification of the crude with acidic agents. While weak acidity is due to the presence of organic acids, such as phenolic or naphthenic acids (found in considerable quantities in the crude oil), strong acidity is attributed to hydrochloric acid which is evolved on distillation of the oil. The potential acidity determines the acid generated in plant distillation equipment.^{96b}

The pH determination of emulsions should also be considered as a part of their systematic analysis. The aging of emulsions very often

causes hydrolysis, which influences the permanence of emulsion systems. The electrometric method of pH determination with a hydrogen electrode is unsatisfactory for emulsion systems. During the procedure, the platinum black electrode becomes covered with a film of the soap present in the emulsion, and this changes the equilibrium potential completely; measurements of this kind cannot give correct values for the hydrogen concentration. The pH measurements of emulsions, such as octane-Stanolox-sodium oleate-water systems, were made by using the quinhydrone electrode,³ and the results show that erroneous values are often obtained. The Beckman glass electrode meter is considered to be the most useful.

When oils are acid-treated to remove undesirable hydrocarbons, the acid is washed out and the oil neutralized. This acid treatment is often the source of certain sulfo- compounds which remain in the oil if not properly refined. When an emulsion determination is made in the absence of these acid compounds, a clean separation between the oil and the water is obtained, while a curdled mass floating on the milky water layer is an indication of their presence.

Certain kinds of engine and machine oils, as well as lubricating oils, which have been treated with acid during the refining process, may contain acid in the final commercial product because of improper refining. The proportion of acid in any lubricating oil should not exceed 0.3 per cent; and when properly refined, the oil should show no trace of sulfuric acid. The proportion of fatty acids contained in vegetable and animal oils may run from 0.5 to 60 per cent. Organic acids may be present in some petroleum crudes to the extent of 0.3 per cent expressed as a sulfide, or 2.1 per cent expressed as oleic acid.

The A.S.T.M. Test Method D47-18 for determining acidity consists in weighing 10 grams of the oil to be investigated in a flask to which is added 50 cc of 95-per cent ethyl alcohol, and neutralizing with a weak caustic soda solution. The flask is heated to the boiling point, shaken to dissolve completely the free fatty acids, and the solution titrated while hot with aqueous 0.1*N* alkali free from carbonate, using as indicator phenolphthalein or methyl orange. The following equation is used to express the results in percentage of oleic acid:

$$1 \text{ cc of } 0.1N \text{ alkali} = 0.0282 \text{ g of oleic acid.}$$

The chlorides of calcium and magnesium and sodium sulfate are the most common salts for which determinations are made. With respect to solids, the determinations involve estimating the total ash, the water-soluble solids, and the centrifugeable solids.

Determination of chlorides is carried out by titration, using silver nitrate with potassium chromate as indicator (Mohr's method^{90c}); thus the red silver chromate indicates the end point (sulfides, mercaptans, or saponified organic acids will obscure the end-point and cause errors in the results). Volhard's method, which is preferred, consists in adding

an excess of silver nitrate and titrating back with potassium thiocyanate, using ferric alum as an indicator. Total chlorides are calculated as sodium chloride. The Volhard method is carried out in acid solution and avoids many of the difficulties of the Mohr method.

Electrometric titration of the aqueous extract, although more tedious, is available by using a silver wire electrode and a potassium nitrate bridge to the calomel cell. This is the most accurate method.

Standard methods for calcium and magnesium estimation are the oxalate precipitation for the first and the phosphate precipitation for the second. These methods are well described by Hildebrand and Lundell.^{56a} Calcium oxalate may be titrated with potassium permanganate, and for magnesium the γ -hydroxy quinoline method has been suggested.^{66a} These determinations have proved to be quite accurate.

A standard barium precipitation method^{96c} has been used to determine the sulfate content.

Scheen and Kahler^{101a} recommended the hydroxyquinone method, which proves suitable for pure sulfate solutions only, but does not give definite end points in the case of extractions of crude oils.

The solid impurities of an oil sample, as stated above, are estimated in three ways. The first is carried out by determining the total ash. Roberts finds that the following procedure works satisfactorily: A sample (50-200 ml) is evaporated in a beaker to the extent of being transferable into a 35-ml porcelain crucible, when it is allowed to sinter until a porous carbonaceous mass has been formed. Concentrated sulfuric acid (2-5 ml) is added to the cold mass and the mixture ignited. The carbon is burned off and the chlorides converted into the non-volatile sulfates. If solids are inorganic salts dissolved in water, the determination is carried out by evaporating the extract to dryness, adding a few drops of sulfuric acid, and igniting the residue to constant weight. The suspended material is best determined by diluting the oil with suitable solvents and then centrifuging the mixture,^{96a, 96b} after which it is treated for soluble salts.

Dougherty³⁰ described a method for determining chlorides in petroleum. The salt is estimated after burning off the oil. From 10 to 20 g of oil are weighed in a dry nickel dish of 250 cc capacity and the dish and its contents are heated over a Bunsen burner. When the oil fumes thickly, the gases above the dish are ignited with the flame and the heating continued until the oil fumes burn off. The Bunsen burner is withdrawn, 75 cc of water are added, and the mixture boiled vigorously for a few minutes. The dish is cooled in a container with cold water until cool enough to handle, and the contents filtered and washed several times with water. A few drops of 1:10 potassium chromate solution are added and the filtrate and washings titrated in the usual manner with a standard silver nitrate solution. The results are calculated to sodium chloride. This method is not very accurate. Matthew's⁷⁵ developed a method of

determining chlorides in petroleum, using acetone for extraction, which has the advantage of permitting the use of larger amounts of oil.

The U. S. Bureau of Mines Method No. 300.2 for the determination of sediment is given in detail in Bureau of Mines Technical Paper No. 323B. It determines gravimetrically the sediment insoluble in benzene, which is in the form of particles sufficiently coarse to be retained in a porous filter. Crude oils, except a few sump hole oils, usually contain a very small amount of sediment, and therefore this test is mostly used for the determination of sediment in heavier grades of fuel oil.

A method for the determination of suspended solids in crude oils has been described by Roberts, Stenzel and Eberz.^{96b'} The centrifugeable solids in a crude oil are determined by diluting the latter with suitable solvents and then centrifuging the mixture. The procedure of this method, which has been found very accurate, is as follows: 50 ml of oil are placed in each of eight 100-ml centrifuge tubes, filled with xylene, shaken, warmed to 140° F, and centrifuged for 10 minutes at 1800 r.p.m. The liquid is decanted without disturbing the precipitate, which is then transferred with the aid of xylene to a single centrifuge tube. The precipitate is then washed with (1) xylene, (2) acetone, and (3) water, and transferred with the aid of acetone to a filter paper previously washed with acetone, dried, and weighed. The filter is then dried for an hour at 220° F and weighed, and the weight of the solids calculated. A portion of the solids is heated in a platinum crucible with a few drops of sulfuric acid, ignited in order to determine the amount of organic matter, and the weight of the mineral portion of the solids (as sulfates) recorded.

Oil

The determination of oil in emulsions of the oil-in-water type with soap as emulsifier consists in determining the oil plus the fatty acids of the soap, by treating the emulsion in a Babcock flask with sulfuric acid. The liberated mixture of oil and acid is centrifuged and measured, its specific gravity taken and the combined percentage calculated. On a separate portion of the emulsion the fatty acids are determined by breaking the emulsion in a separatory funnel with alcohol and petroleum ether, shaking out the soap with several changes of alcohol, evaporating the alcohol and recovering the fatty acid from the residue by decomposing with acid. The fatty acids are extracted with ether and the residue evaporated to dryness and weighed. The percentage of fatty acid obtained is deducted from the combined percentage previously found and the percentage of oil obtained.

Markwood⁷⁴ considered this method tedious, requiring several hours. The other disadvantages which he pointed out are that it is indirect and also makes use of inflammable, volatile solvents. He proposed a direct method that can be completed in 20 to 30 minutes with no inflammable solvents involved. This method is based on the fact that emulsions of the oil-in-water, soap-stabilized type are resolved by phenol, which has the ability to alter the surface tension of a soap solution. This method

consists in weighing a portion of the sample (about 5 grams), introducing it through a tube into a 10-cc calibrated flask and adding dropwise 3 cc of a phenol solution (75-per cent). The flask is rocked gently back and forth and rotated in order to bring the phenol into contact with all portions of the emulsion. To complete the resolution, another cubic centimeter of phenol may be added slowly. The cylinder is then centrifuged for several minutes and the volume of the oil layer read. The specific gravity of the oil is determined in a small pycnometer and the percentage of oil calculated. The volume of phenol is limited to about 4 cc when using a 10-cc graduate. The method may be modified by using the usual Babcock flask in place of the graduate. In this case the oil sample is increased to 10 grams, and a larger area of contact of the emulsion and phenol obtained; this is essential in handling stubborn emulsions. After the emulsion is completely broken, water is added slowly down the side, without mixing the contents, until the volume of oil may be read in the graduated portion, thus the oil is subjected to a washing process and the small amount of phenol dissolved therein is removed. In the case of the Babcock flask, as much as 15 cc of phenol has been used on a 10-gram sample. This is an extremely inaccurate method because of the relatively high solubility of phenol in the oil.

A rapid graphical method for the determination of the proportion of crude oil in water-in-oil emulsions, where the character of the crude oil and the composition of the oil-well water is known, is described by Wischetravsky.¹²³ A curve is constructed on a chart which indicates the specific gravity of the crude oil and the bore hole water in various known proportions. To determine the oil content in an emulsion obtained from the same bore hole, only a specific gravity determination is required, the proportion being interpolated from the curve.

The gravity of the dry oil may be determined by using Woelflin's chart,^{125a*} which is based on calculated values, since there is no change in volume during emulsification. The wet oil may also be resolved into oil and water, and the gravity of the separated oil measured by means of a hydrometer (ASTM Method D 287). The national Standard Petroleum Oil Tables, U. S. Bureau of Standards Circular (N154) may be used to correct the observed gravity at the observed temperature to the gravity at 60° F.

Woelflin † compared three methods used for determining *gravity of the oil component* of cut oil. These methods are: (1) distillation, (2) computation, and (3) chemical-centrifuge. In the first method, oil is distilled at a temperature sufficiently high to remove the water, and the water and distillate are condensed in an ice bath. The distillate is separated and poured back into the residue, vigorously stirred, and the gravity of the resulting mixture determined. The distillation method has been discarded because of two sources of error. The first is that

* Woelflin's chart may also be used to determine any one of the following properties: gravity of the brine, percentage of the brine, and percentage of oil.

† *The Electric Dehydrator*, Vol. 2, No. 3, March, 1932.

some of the light oil fractions escape the condenser and this results in a loss of gravity. The second is that if water were very finely divided in the cut oil, the salt remaining after evaporation of water would be of an extremely small particle size and would remain in suspension. This suspended salt would also cause the gravity of the oil to be too low.

The calculation method has been found correct only in case the amount of water present in the cut oil does not exceed 3 per cent (the error is not over 0.1° A.P.I.). Calculations for correcting the gravity of a crude oil for water content are usually made at the observed temperature of the cut oil. A sample computation, correcting the gravity of a Signal Hill oil having a water content of 2 per cent, is given by Woelflin:

Observed gravity of cut oil, 28.7° A.P.I. at 65° F =	Sp. gr. 0.8833 at 65° F
Water content by distillation or by chemical, 2.0% water	
Sp. gr. of water 1.0165 at 79° F =	1.0180 at 65° F
Weight of 100 ml of cut oil at 65° F =	88.33 grams
Weight of 2 ml of water at 65° F =	2.04 grams
<hr/>	
Difference is weight of 98 ml of oil =	86.29 grams
Sp. gr. of oil at 65° F =	86.29 ÷ 98 = 8809
*A.P.I. of oil at 65° F =	29.1
*A.P.I. of oil at 60° F =	28.8

Finally, the chemical centrifuge method is considered most satisfactory and, when used in conjunction with the calculation method, permits the determination of gravity at any desired cut. The "chemical-centrifuge gravity" is obtained by adding a small amount of de-emulsifying chemical to the cut oil to break the emulsion and centrifuging out the water. The gravity of the separated oil is then determined by a hydrometer or Westphal balance.

A 100-ml centrifuge tube is used for the cut oil. About 2-10 drops of the chemical is added, and the tube is stoppered, shaken, and centrifuged. Use of the same kind of chemical which serves to break the emulsion in the field is recommended. When the gravity of the oil is below 22° A.P.I. the tube, after shaking, is placed in a water bath (100-130° F) for 30 minutes before centrifuging. The oil is centrifuged for $\frac{1}{2}$ to 4 hours. If previously heated, the oil is cooled to room temperature. If the oil is of high gravity, lighter than 26° A.P.I., it is removed from the tube with a pipette. About 150 ml are necessary when using a 6-inch hydrometer. After determining the gravity, a cut is taken of the oil to determine the water content.

Water

The existence of numerous methods for determining the water content of oils and emulsions indicates the importance of this determination. There are two principal test methods for determining water, both in the laboratory and in the field: (1) determination of emulsion water and sediment (BS&W) by centrifuge; (2) determination of water by distillation.

The determination of BS&W by centrifuge shows the amount by volume of emulsion, water, and sediment. This is the simplest and most rapid method of determining the water content (Refer to ASTM Method D 96-30).

The centrifuge method consists in placing 50 ml of 90-per cent benzene and 50 ml of the oil to be tested in 100-ml centrifuge tubes shaking vigorously, heating to 120° F for 10 minutes, and again shaking and centrifuging. The emulsion water and sediment are thus precipitated. A better solvent than benzene was selected for asphalts and waxes present in the oil, namely, diethyl ether, as well as 3:1 mixtures of gasoline-carbon disulfide, gasoline-diethyl ether, and petroleum ether-benzene. In the centrifuge tests on wet oil, it has been suggested adding to the centrifuge tubes before heating a few drops of a demulsifying agent, such as Tretolite, whereby the total water content of wet oil is obtained as the emulsion resolves into oil and water. (ASTM method D 96-30).

The distillation method for determining water in emulsified oil consists in refluxing a measured quantity of oil mixed with a diluent and collecting the distillate in a graduated receiver. The water content determined by this method should be corrected for the difference between the volume of salt water present in the wet oil and the volume of the distilled water measured in the receiver. This correction varies from 0 to 8.2 per cent (for water containing 20 per cent salt). (ASTM Method D95-30.)

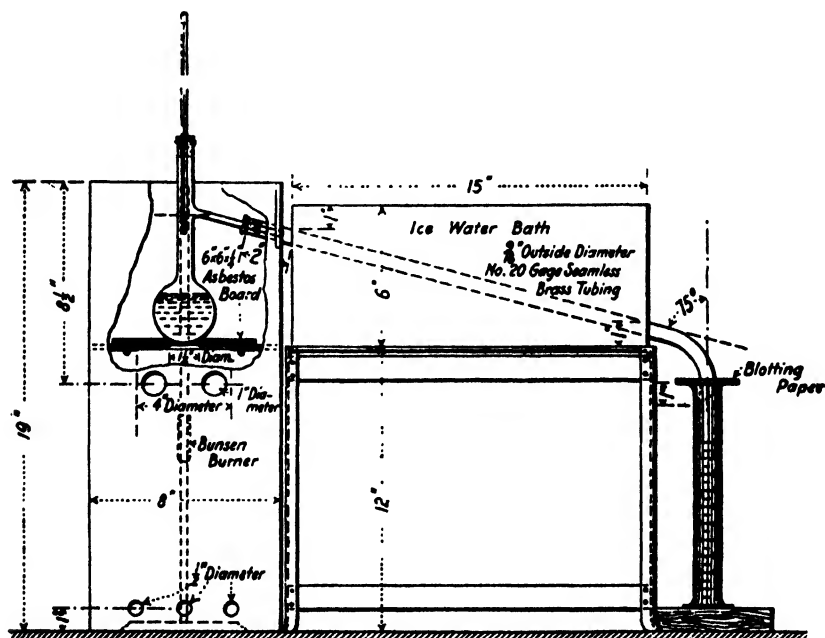


FIG. 33a. Apparatus for Distillation Test.

According to the ASTM Method D 95-30-100 ml, (IPT) Serial Designation F014, a metal still is used in distilling cut oils having a high water content. In the standard method for testing water, the oil is dissolved in an equal volume of gasoline of a specific boiling range and distilled in a modified Dean and Stark apparatus. The still is a round bottom 500-ml flask fitted with a reflux condenser discharging

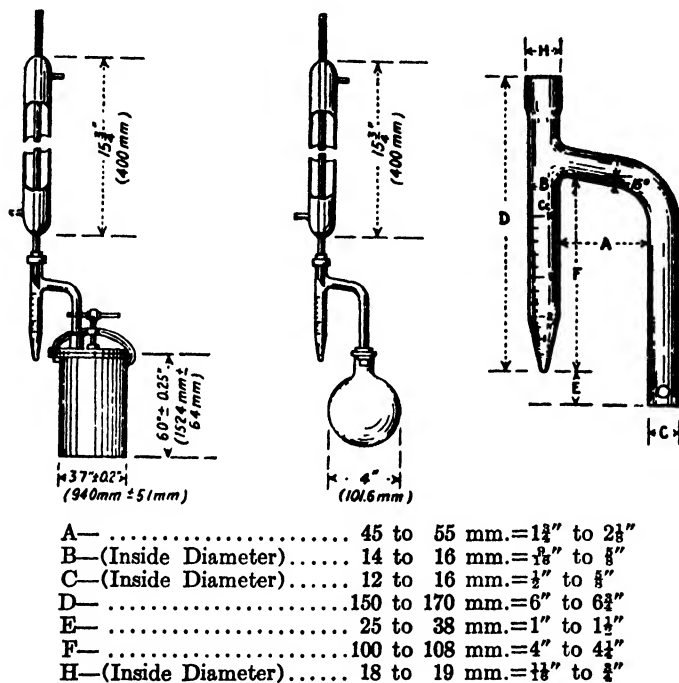


Fig. 33b. Apparatus for Determining Water.

into a glass trap which serves to collect and measure the water, while the excess solvent is returned to the flask. Water-saturated xylene may be used as a solvent, and the addition of one per cent of triolein has been recommended to reduce foaming.

Senger¹⁰⁶ determined the proportion of water admixed with tar by slowly inserting into it a glass tube about 8 mm in diameter, withdrawing the tube, and calculating the amount of water from the length of the column in the tube. After pouring off the water, the sample is mixed in a mortar and 500 g are distilled in a copper container of one liter capacity, the removable lid of which is fastened by clamps. The steel-encased container is heated by gas until the water is completely boiled off. The oil starts to distill at about 200° C. This determination takes about 3 to 4 hours, and no foaming occurs.

Testori¹¹⁷ determined water in molasses by distilling about 50 g of molasses with 200 cc of turpentine and collecting the condensed water in a

graduate. This procedure has been claimed to be more accurate than ordinary oven drying. Jayne⁶⁴ used an improved testing still of heavy copper with straight sides, which is easy to clean thoroughly.

Sadtler¹⁰¹ used a distillation method to determine water, especially in tars. Because of the particularly viscous character of tars, lumping and frothing is very likely to occur on distillation.⁶⁴ The carefully sampled substance (25 to 50 g, depending on the moisture content) is quickly covered with 200 to 300 cc of benzene in an Erlenmeyer flask which is connected to a Liebig condenser, and a receiver, similar to that adopted by Dean, and consisting of a tube of about $\frac{1}{8}$ inch inside diameter graduated in tenths of a cc, is placed in position. At a little above the 10 cc mark the tube is drawn into a funnel or bulb shape large enough to hold 250 cc. Sadtler recommends first heating, not distilling, the benzene in the flask by means of an oil bath at a temperature of about 110 to 120° F for from one to two hours when the water collects in the upper part of the flask and condenses. Distillation begins after one to two hours of heating and runs regularly at a rate of about one drop per second. The water distills over before the benzene gets too hot, and the latter does not apparently emulsify with the water to any great extent while distilling.

Some tars are very difficult to free from water and tend to boil over. Jayne⁶⁴ suggested that the removal of water might be greatly facilitated by adding to the tar a hydrocarbon, such as pure toluene, boiling at a temperature slightly higher than water. Partly because of the viscosity of the tar and partly because of the small difference in specific gravity between water and tar, the water determination is quite difficult. The addition of toluene thins the tar and, as distillation proceeds, the water is almost completely carried over. Jayne points out that distillation for determining water content, which otherwise requires hours, can be completed in this way in about twenty minutes.

Marcusson⁷³ proposed a method for the determination of water in oils, fats, soaps and resins by distillation with an immiscible liquid. Water-saturated xylene has been used as the liquid to carry over the water in distillation, the water being collected in a 100-cc graduate. The method is rather inaccurate. In the Charitschkoff method, 100 g of petroleum are diluted with 500 cc of kerosene previously saturated with water. A part of the mixture is introduced into a 100-cc tube, shaken to obtain solution of the petroleum in the kerosene, and allowed to stand 24 hours until complete settling of the water takes place.

Dean²⁵ attempted to estimate the moisture in creosote oil, using Marcusson's method, and claimed more accurate measurements of the condensed water. Graefe⁴⁰ determined the moisture in lignite by distilling with naphtha. Hoffman and Marcusson⁵⁷ also suggested a method for the determination of water in tars in which the oil is diluted to one-half with a light oil, boiling from 80 to 120° C, and is then distilled. It is pointed out that a graduate which is narrow at the bottom be

used to allow a more accurate reading of the water separated by distillation.

A method for determining the water content, applicable to coal tars which cannot be handled by other methods, is described by Prutzman.⁹⁰ He uses an apparatus consisting of a pint-size oxygen retort, with a bent outlet tube connected with a straight tubular condenser. (Between the collar of the retort and the still head is an asbestos gasket filled with graphite grease). A sheet-iron jacket surrounds the bulb of the retort, and a tapered centrifuge tube is used as a receiver. A fifty-fifty mixture of benzene and toluene is used as a reagent. Fifty cc of oil and 50 cc of reagent are measured and poured into the bulb of the retort. On distilling, benzene and water are driven over, followed by toluene, which forces the condensed water out of the neck and condenser into the centrifuge tube. The volume of water is read off and calculated in the usual manner. With very strongly emulsified oils, or where the percentage of water is very high, Prutzman recommends using a two-pint retort bulb and double the amount of the benzene mixture. The extreme solubility of petroleum in benzene and toluene, and the low boiling point of benzene, prevent the samples from foaming over. The Transport Co. of West Virginia also proposed a method of water determination by mixing an average sample of oil with an equal quantity of benzene and subjecting the mixture to a temperature of 120° F for not less than 2 hours for light grade petroleum, and about 18 hours for heavier grades. The following scale, based on density, evaluates grades of petroleum:

Grade: A.	37.1	Density:	0.838
B.	33.0-37.0		0.859-0.838
C.	31.6-32.9		
D.	30.6-31.5		0.872-0.867
E.	29.6-30.5		0.877-0.872
F.	28.6-29.5		0.883-0.877
G.	28.5		0.883 or more

Spalteholz¹¹⁰ uses an iron kettle of one-half liter volume for determining water in tar. The kettle has a side outlet near the top and four openings in the cover, one for a thermometer, one connecting with the side outlet, one for a condenser, and one for a dropping funnel. The funnel discharges into a small cylindrical reservoir which overflows into the kettle. To make the determination, the kettle is filled with high-boiling anhydrous anthracene oil, heated to 270°, and the tar sample is allowed to drip slowly from the funnel into the hot oil. The low-boiling part escapes through the side outlet, the water through the condenser. (It is claimed that the apparatus requires no filling after a test run and permits rapid and sufficiently accurate work.)

A method for the determination of emulsified water in greases and coal-tar samples has been worked out by Dean and Stark.²⁷ Naphtha solvent proved useless for this type of emulsion, since the tars in question were quantitatively insoluble in petroleum distillates. When petroleum emulsions were tested, the xylene-benzene-solvent mixture was found to

work satisfactorily. In estimating the water content of various organic emulsions, particularly of petroleum emulsions, the method for distilling in the presence of an immiscible solvent was considered the most reliable. A mixture of 80 per cent of commercial xylene and 20 per cent of commercial (90-per cent) benzene was the solvent used. To avoid bumping (in which oil is blown out through the top of the condenser), a porous plate is used during distillation. The procedure is as follows: 100 cc of the emulsion is placed in a graduate with 100 cc of the solvent. The emulsion is poured into a 500-cc flask, drained for 1 to 2 minutes, and washed with successive portions of the solvent. Distillation proceeds at a rate of 2 to 4 drops per second for one hour. A special type of electric heater, similar to the one described by Dean²⁸ was used by these investigators, but without regulating rheostats. (The resistance element operates on a 110-volt alternating current, and is constructed of No. 27 nickel-chromium wire 23 feet long. It has an approximate resistance of 72 ohms and a capacity of 165 watts, which maintains the desired rate of distillation). Among other solvents, the so-called cleaners' naphtha, derived from petroleum, is claimed to work very satisfactorily. The advantage in using a solvent not miscible with water is the prevention of foaming.

In Barrett Company's method described by Weiss, 200 cc of the emulsion are mixed with 200 cc of light oil and distilled at 400° F. The water is collected and measured. This method of determination requires considerable time and attention on the part of the operator.

Nettel⁸¹ described an interesting method of water determination. One hundred cc of oil-containing water are mixed with an equal volume of light benzine and 50 cc of 0.1*N* hydrochloric acid is added. By shaking for 5 minutes in a separatory funnel the hydrochloric acid absorbs the water, and after standing a half hour at 65° it separates to a large extent. The water absorbed by the acid is determined by titrating with 0.1*N* sodium hydroxide. According to Nettel, the water is absorbed completely by the acid and the oil is not changed chemically. Since the water in the crude is considered neutral, it has no influence on the method. Actually, oil-field lines vary between pH 5 and pH 12.

Differences between the percentage of water obtained by distillation of a given oil are often quite significant, for example, 1 per cent instead of 0.7 per cent (Nettel method). There may be various reasons for such a disagreement, for instance: (1) In the case of petroleum an unequal distribution of water in oil may be the result of a difference in sampling; and (2) During the time of shaking with the reagent, not all the water droplets are brought into contact with the added substance which extracts the water. On the other hand, the investigations of Engler reveal that nitrogen-containing substances of the pyridine series are present in crude petroleum, which react with hydrochloric acid if it is used for treating, as in the Nettel method, thus leading to a higher value of water content. In addition, any other substance which reacts with hydrochloric

acid will lead to high results, and any alkaline material present in the system will lead to low results.

Graefe's ⁴¹ method for water determination is based on the reaction of metallic sodium with water. The oil is not diluted with benzene because such dilution accelerates the precipitation of water and does not allow complete contact of the alkali metal with the water. Only a liquid which dissolves water may be used for this purpose, *e.g.*, ether, which must be free from water and alcohol and previously dried over sodium. The sodium powder is prepared by melting sodium in a flask filled with xylene and shaking until it solidifies. Graefe's apparatus consists of a small (30- to 40-cc) distillation flask containing 5 to 10 cc of ether. By means of a wide-neck funnel a half teaspoon of powdered sodium is introduced and quickly washed with 10-20 cc of ether. A small separatory funnel drawn to a narrow tube extends into the ether layer and is securely fastened to the flask. About one cc of the crude oil is poured into the funnel, washed with one cc of ether, and stirred with a platinum wire to lower viscosity. The stop-cock of the separatory funnel is opened to permit the crude oil to flow into the flask. Hydrogen is set free when the first drops of oil flow on the sodium. Since the hydrogen evolved contains ether vapors, thereby increasing its volume, it must be adsorbed. The completeness of water decomposition is calculated from the gas volume increase. According to the reaction: $2\text{Na} + 2\text{H}_2\text{O} = 2\text{NaOH} + \text{H}_2$, or one H_2 requires $2\text{H}_2\text{O}$, it is known that 1/1000 gram molecule of H_2 occupies a volume of 22.38 cc at 760 mm pressure and 0° and requires 36 mg of water for its formation. Each cc of H_2 corresponds to 1.61 mg of water at 760 mm and 0° . Calculations are made using the formula:

$$\frac{a \cdot 1.61 (b - s) 273}{760 \cdot (273 + t)} = \text{mg H}_2\text{O}$$

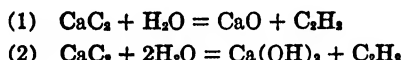
where a is the number of cc of H_2 , b the barometric pressure in mm of mercury, s vapor tension, in mm of mercury, of the naphtha used in the burette, and t the temperature in degrees centigrade. The vapor tension of the naphtha used is so small that it is practically negligible.

Graefe points out one objection to this method, namely, that hydrogen is also formed from other substances in the crude oil, but only hydroxyl and carboxyl groups containing compounds can be taken into consideration. From phenols, only one hydrogen is set free, according to the equation: $2\text{ArOH} + 2\text{Na} = 2\text{ArONa} + \text{H}_2$, where Ar is an aromatic radical whose molecular weight is about 5 times that of water, so that only $\frac{1}{5}$ as much hydrogen is evolved. Further, phenol occurs only to the extent of a fraction of a per cent in petroleum; its influence may therefore be neglected. In the case of tars and brown coal tars, Graefe's method is unsuccessful. Carboxy-acids react with sodium after completion of the reaction with water, thereby liberating additional water which reacts with the excess sodium, liberating additional hydrogen. (A solution of stearic acid in ether required about 24 hours for complete conversion.)

Graefe also tried a method of determining the water content by the difference in specific gravities of oil containing water and water-free oil. About 100-cc samples of crude oil were put into tightly closed bottles containing about 20 g of anhydrous calcium chloride. The bottles were allowed to stand in a steam bath for many hours. The water-free oil, as well as that containing water, was weighed after standing over night. The amount of water obtained was much higher than that found by other methods. The apparent sources of error are (1) precipitation of organic acids by reaction with calcium chloride; (2) removal of high molecular weight and/or polar materials by adsorption on calcium chloride; and (3) losses by evaporation.

Charitschkoff,¹⁸ and later Robert and Fraser,⁹⁰ proposed a chemical method for the determination of water in petroleum, based on mixing a weighed amount of petroleum with calcium carbide. According to the equation: $\text{CaC}_2 + \text{H}_2\text{O} = \text{CaO} + \text{C}_2\text{H}_2$, acetylene is generated and measured. The determination, according to this method, requires only about 15 to 20 minutes.

The acetylene method was further developed by Strache and Glaser,¹¹⁵ who proved that the formation of acetylene from calcium carbide and water proceeds according to the following equations:



Up to 40°, the reaction follows equation (2); from 40-140°, both reactions occur simultaneously; above 140°, the reaction follows only equation (1). Strache and Glaser¹¹⁵ did not measure the acetylene formed, but they did determine the heat of combustion with a direct-reading bomb calorimeter constructed by Strache. This method worked well for the determination of comparatively small amounts of water and water vapor in air and gases, but was modified for the determination of water in emulsions. The dried air was conducted through the heated emulsion as in the case of the analytical weight method, except that the air was passed over calcium chloride in a tube placed in a bath held at a fixed temperature. This was done to differentiate between the two reactions. A diagram (refer to the original work of Strache and Glaser) is presented summarizing the percentage of water vapor reacting according to equation (1) and equation (2) for all temperatures. This allows direct determination of the water content from the amount of acetylene formed.

Allen and Jacobs,² in a paper presented at the Eighth Congress of Applied Chemistry in Washington, discussed the Wielezinski and Robert and Fraser method. They suggested that the acetylene evolved should be measured by displacement with a saturated solution of sodium chloride, in which it is insoluble.

Sselski¹¹² advises the use of a centrifuge in connection with the method of water determination based upon its separation by settling out from a benzene solution. This method was developed by Dean, Stark, and also

Marcusson. By using a centrifuge, separation of water and benzene is obtained in a short time. The usual settling test, known as the Accisen Method, can be improved, according to Sselski, if, after the water has collected in the lower part of the benzene-oil solution, leaving the upper layer practically free from water, the top layer is poured off and the remainder diluted with benzene.* This may be repeated several times. Sselski notes that there is a better separation in the less viscous and lighter benzene than in the more viscous petroleum. The centrifuge method at the same time also allows for the determination of impurities present in the form of mechanical admixtures. This method does not work with crude oils diluted with benzene (Woelfin, *Electric Dehydrator*, 1932-1933). Treating chemicals should be added to benzene in order to resolve emulsions to water, or phenolated benzene should be used as a cutting solution.

Odell and Thiele⁸⁵ mention a method frequently used for petroleum emulsions, which requires the addition of a light gasoline. Dilution with an oil which dissolves much less water than gasoline is difficult. Gasoline dissolves an extremely small amount of water, and is often used to precipitate water quantitatively from other organic liquids. In this method the mixture is centrifuged, and the water settles at the bottom, its volume being read directly. The next procedure is centrifuging with a heavy solvent which has a high specific gravity, is a good solvent for tar, and is immiscible with water. Carbon tetrachloride and carbon disulfide are such solvents, the former being preferable. Actually none of the solvents named can be depended upon to resolve crude-oil emulsions to water. It is stated that warming the solution before centrifuging aids in the separation, and that this method is more accurate for a small percentage of water in the emulsion than for large amounts (75 per cent).

Odell and Thiele⁸⁴ proposed a method involving selective adsorption of water from a vaporized sample by suitable reagents. Carbon black, for example, has a very strong adsorbing power for oil and tars. The amount added depends on the character of the oil or tar (about one-fifth by weight of the tar used). It is stated that a tar emulsion is resolved by addition of carbon black, permitting the free water to unite and separate. The accuracy of the method is claimed to increase for large percentages of water. Since no mention is made in the literature of the use of any other dehydrating agent, and since carbon black should stabilize, rather than break, an emulsion, the method does not seem to be feasible. Distillation methods work easily and quickly for tars having a small amount of water, but otherwise these methods are tedious.

For oils containing phenolic substances and light-colored shale oil, as well as for coal-tar distillates, the sulfuric acid dehydration method is applicable. The simplest among such methods is the shaking of a known volume of oil in a stoppered graduate using concentrated sulfuric

* The method of pouring off the top oil should not be used, as a considerable proportion of the fine emulsion which has not been precipitated will be lost (Roberts).

acid ($\frac{1}{10}$ by volume proportion of acid to oil). The amount of water present is determined from the contraction in the volume of the oily layer. The method is limited in its application, because most of the oils are sulfonated by agitating with sulfuric acid, although frequently the water present in the oil reduces the strength of the acid and makes the amount of sulfonation negligible. This method is considered useful for the rapid estimation of water present in the oil, and it is claimed to serve for the determination of water in tars containing not more than 10 per cent.

Another method recommended by Odell and Thiele⁸⁴ is the Latex-copper sulfate method, which is more accurate. Five grams of oil are weighed in a beaker which is covered with a slightly greased watch glass. One to two grams of pure copper sulfate are ignited to the white anhydrous salt and cooled in a desiccator. The weight of the anhydrous salt is determined and the content of the crucible added to the oil in the beaker. The oil is dissolved in 70 cc of a suitable anhydrous solvent, agitated for some time, and allowed to stand for a few hours. The lumps of copper sulfate are filtered off and washed with a light solvent, and the latter is evaporated. The gain in weight of the copper sulfate represents the amount of water in the 5 grams of oil taken. This method is especially useful for spent benzene, wood tar with a high water content held in suspension by phenolic substances, and similar compounds which, acting as emulsifying agents, permit the emulsification of large amounts of water in the oils named.

An accurate method for the determination of water in gasoline and benzene, whether present in solution or in suspension, is the calcium chloride method proposed by Clifford.²⁰ (The Graefe method has been found to be unsuitable for the determination of water dissolved in gasoline.) With respect to other solvents, such as acetone, pyridine, ethyl alcohol, and glycerol, it is stated that they cannot be analyzed for their water content by the calcium chloride method, as they are miscible with water; they are retained by calcium chloride only to a certain extent and therefore cannot be displaced. This method is unsatisfactory, not only for liquids which are completely miscible with water, but because there seems to be a reaction between calcium chloride and the organic liquid, and/or an absorption of alcohol or crystallization. The calcium chloride method works as follows: a current of air, previously dried by calcium chloride, is passed through or brought into contact with the sample in question at the rate of 5 to 15 liters per hour for from 1 to 2 hours. If a part of the water settles, it must be shaken frequently to keep it in suspension; complete vaporization of the water must be secured. The moisture extracted from the sample by air is adsorbed in another calcium chloride tube. To displace the vapor from the tube before weighing, dry air is passed directly from the calcium chloride tube at the rate of 5 liters per hour for one hour. Any other suitable dehydrating material may be substituted for calcium chloride, but it must not absorb or react with the vapor of the sample.

There is also a method of freezing out water by subjecting the emul-

sion to a low-temperature bath; however it is impractical for determinations of water in crude petroleum, as well as for water dissolved in gasoline, since calculation is based on the difference in the specific gravities of the sample before and after dehydration. Emulsified crude oils are not in general susceptible to dehydration by freezing and the method is also too cumbersome for general use.

The standard procedure* for freezing emulsions is carried out as follows: About 400 g of an emulsion are placed in a clean metal container, such as a one-pint press-top tin, the container sealed, and the emulsion exposed to a temperature of 0° F (−17.7° C) for 12 hours, after which it is permitted to thaw by exposure to room temperature. This alternate freezing and thawing is repeated twice after the first operation (three cycles of freezing and thawing). The result of this test is that the emulsion either appears homogeneous after the third cycle or is broken and separated into distinct layers.

Rosewarke and Connell⁹⁸ report a suitable method for determination of the water content on a small, as well as on a large, laboratory scale, based upon the effect produced by allowing the material to flow onto a hot surface in a closed space. This method has been used for separating water from stiffly mixed Alberta bituminous sand emulsions. The apparatus consists of a 5 liter "Pyrex" flask with a special short still head, carrying a copper funnel 17 inches in diameter. The upper part of the funnel is heated with gas to produce a ready flow (regulated by a valve) of the bitumen. The flask is placed on a sand bath and heated, foaming being prevented by maintaining the temperature below that of boiling water. The loss of light oil constituents is determined by means of a charcoal adsorption tube. The difference in the weight of the bitumen charged into the funnel and the final product gives the water content of the emulsion.

Very little information exists regarding the solubility of water in hydrocarbons, such as petroleum, paraffin oil, etc. Among the many methods described by Allen and Jacobs² for the measurement of water in petroleum products, Elisabeth W. Aldrich,¹ considers the methods of Groschuff and Clifford as most accurate for the quantitative determination of water dissolved in gasoline. Groschuff⁴² measured the solubility of water in kerosene, benzene, and paraffin oil by observing the temperatures at which known amounts of the tested substance and water heated in sealed tubes and then cooled revealed the presence or absence of turbidity. This method is erroneous because it is difficult to prevent undercooling and difficult to estimate the total water dissolved since some of it may adhere to the walls of the tube. Clifford's method²⁰ consists in bubbling dried air through water-saturated gasoline and weighing the calcium chloride tubes through which air and vapors were passed. Gasoline vapors were removed by passing dried air through calcium chloride tubes for several hours. In this method a loss of water vapor is possible during

* A.S.T.M. Tentative Standards No. 744 (1936).

the time when water is adsorbed in the weighed tube, since the dried air is diluted with gasoline vapor, thereby reducing the partial pressure of water vapor below 0.2 mm (vapor pressure of water above calcium chloride is about 0.2 mm of mercury).

Miss Aldrich used a modified Clifford method in which hydrogen liberated by sodium was a measure of the amount of water present. The sample of gasoline was saturated with water by shaking for a predetermined period at a constant temperature. The water-saturated gasoline was placed in a container filled with dry air, and a sodium-potassium alloy introduced. The hydrogen evolved from the gasoline and frozen in liquid air was measured in a burette at a definite temperature and pressure. Measurements recorded included data on the volume, temperature, and pressure of hydrogen, and on the weight* of the water dissolved in the known weight of gasoline, as well as in 100 grams of gasoline, computed according to the following equation:

$$S = \frac{57.78 \times 10^{-3}}{W} \left[\frac{PV}{t + 273.1} \right]$$

where S is the solubility in weight percent; P , the pressure of hydrogen in mm of mercury; V , the volume of hydrogen in ml; t , the temperature of hydrogen in °C, and W , the weight of the gasoline sample in grams.

Table 5. Solubility of Water in Gasoline
(Elisabeth W. Aldrich)

Source of Gasoline	Sp. Gr. 60°/60°	Temper- ature of Satura- tion (°C)	Weight of Sample (gr)	Volume (ml)	Temper- ature (°C)	Pressure (mm)	Solubility (Weight %)
Oklahoma natural gasoline	0.677	10	24.04	6.61	31.2	246	0.0128
		30	29.59	8.67	26.0	283	0.0160
		50	21.17	7.87	28.2	271	0.0193
West Virginia natural gasoline	0.695	10	22.01	3.05	31.0	193	0.0051
		30	33.56	4.91	26.0	237.5	0.0067
		50	32.29	5.26	29.5	237	0.0074
California crude	0.733	10	24.66	3.99	29.0	212	0.0066
		30	32.82	4.99	27.0	236	0.0069
		50	20.27	5.44	28.7	215	0.0111
Mid-Continent crude	0.718	10	22.84	3.27	32.0	214	0.0058
		30	31.06	8.67	25.0	295	0.0158
		50	28.41	10.39	27.0	295	0.0208

Groschuff and Clifford found that the solubility of water in benzene is approximately five times greater than in gasoline, and that the temperature coefficient of solubility is much greater than that for gasoline. Similar differences may be anticipated between different hydrocarbon series (Aldrich).

The question of determining water dissolved in oil is important when

dealing with transformer oils. Groschuff⁴² carried out solubility determinations, using Alexejew's method,¹ later perfected by Rothmund.⁹⁹ This method consists in a complete dissolution of water by heating to a high temperature and cooling below the solubility point so that a fine fog is formed. The solubility temperature is determined within 5-10 degrees, the water is redissolved, the fog formed as quickly as possible (not too strong under cooling), and the container placed on a bath at the anticipated solubility temperature. If the fog disappears in 10-15 minutes, or drops of water are formed on the walls of the container, the experiment must be repeated. Groschuff's work shows that at 18° benzene adsorbs 0.057 per cent by weight of water, petroleum 0.005, and paraffin oil 0.003, the solubility increasing with increase in temperature (the temperature coefficient changes likewise). The water content of petroleum and paraffin oil saturated with water is the same as that of air saturated with water, but for benzene it is much higher.

In the case of highly treated oils (those which must be thoroughly cleaned) much trouble is encountered from emulsions and poor washing due to an excessive proportion of water used in washing. It is possible to determine from experiment the proportion of water to oil which gives good washing and a minimum of trouble. In plant practice a fixed minimum of water is pumped in and live steam turned on. The steaming is continued until the water volume is increased to the determined figure, when the steam is shut off and the wash water allowed to settle. In this way it is possible to discount differences in the quality of the steam, as well as seasonal and other temperature conditions which increase or decrease condensation.

Fowler's (H. G.) method of neutralization applied to the washing of oils brings both the matter of temperature and water balance under control. He found that if an acid-treated oil is neutralized with soda in the cold, sufficient soda added to carry the batch to the alkaline side, and the temperature of the oil-soda mixture raised quickly to 180° F or higher, the soaps will break clear, settle rapidly, and give a superior quality of oil. In using this method, it is possible to determine the strength of the soda, the temperature, and the proportion of wash water necessary to give good results.⁴³

APPENDIX

Origin of Petroleum

According to Berthelot, "rock oils" are products resulting from the action of steam and carbon dioxide upon alkali metals, such as sodium. Mendeleef's and Moissan's hypothesis is referred to as the carbon hypothesis. It is believed that petroleum was generated by the action of water upon iron carbide and as a result vapors of petroleum and deposits of iron ore were formed. This hypothesis is derived from the similarity between acetylene and petroleum. The varying composition of crude petroleum is accounted for by varying physical conditions (temperature and pressure) under which the crude oil was formed. But petroleum

crudes are far from having fundamentally the same general composition. The organic origin theory to which many scientists subscribe includes four modifications: (1) dry distillation of marine animals produced the petroleum deposits; (2) vegetable matter has been the basic material; (3) distillation of bituminous coal at high temperature caused volcanic heats, and petroleum vapors were produced and condensed, leaving anthracite as a residue; petroleum deposits may be found, then, either at the place of origin, or in a different location; (4) Decomposition of organic matter (vegetable or animal) under high pressures and comparatively low temperatures. The latter hypothesis is considered the most plausible.

The composition of oils obtained from various fields is as follows:

- (1) Mid-Continent Field: mixture of paraffin and other less important series of hydrocarbons.
- (2) California: olefin, naphthene, and paraffin hydrocarbons.
- (3) Appalachian Field: paraffin hydrocarbons.
- (4) Wyoming: paraffin hydrocarbons.
- (5) Illinois: mixtures of olefin and paraffin hydrocarbons.
- (6) Mexico: mixtures of all kinds of hydrocarbons.

Naphthene hydrocarbons, (C_nH_{2n}) $n = 1-15$, predominate in California, Russian, and Japanese oils.

Physical Properties of Petroleum Indicating its Source

Engler³¹ states that the most characteristic physical properties indicating the locality from which an oil is obtained are refractive index and specific gravity.

Table 6

	Fraction 140-160°		Fraction 190-210°		Fraction 240-260°		Fraction 290-310°	
	Sp. Gr.	Ref. Ind.	Sp. Gr.	Ref. Ind.	Sp. Gr.	Ref. Ind.	Sp. Gr.	Ref. Ind.
Pennsylvania	0.7550	1.422	0.7860	1.439	0.8120	1.454	0.8325	1.463
Baku	0.7820	1.436	0.8195	1.454	0.8445	1.467	0.8640	1.475

1. Specific Gravity

The approximate specific gravities of various American crudes follow:

Table 7

Field	Baumé Gravities	Specific Gravities
Lima, Indiana	35-40	.8484-.8235
Illinois	28-40	.8860-.8235
Mid-Continent	28-40	.8860-.8235
Colorado	30-32	.8750-.8641
Gulf	14-25	.9722-.9032
California	12-30	.9850-.8750

The A.P.I. gravity scale is an arbitrary one which is related to the specific gravity of a petroleum oil in accordance with the formula:

$$^{\circ}\text{A.P.I.} = \frac{141.5}{\text{Sp. Gr. } 60^{\circ}/60^{\circ} \text{ F}} - 131.5$$

In volume II of "The Science of Petroleum," D. W. Gould^{39a} gives a gravity correction table which offers a ready means of converting specific gravity into degrees A.P.I. (A.S.T.M., Bureau of Standards, Serial Designation D287-37).

The specific gravity of most crudes lies between 0.80 and 0.95 (54.4 and 17.4 ° A.P.I.)

Table 8. Gravity of Various Classes of Crudes

Type of Base	Class of Crude	Sp. Gr. 60°/60° F	° A.P.I.
Paraffin		0.781	49.7
Paraffin intermediate	Oklahoma	0.829	39.2
Intermediate	Oklahoma	0.827	39.6
Intermediate naphthene	Wyoming	0.964	15.3
Naphthene	Texas	0.879	29.5
Naphthene (wax-free)	Texas	0.910	24.0

Density is weight per unit volume and specific gravity the ratio of the weight of an equal volume. Methods used for their determination are: (1) pycnometer method based on the direct weighing of a known volume of the substance; (2) density balance or Westphal balance method based on the loss of weight of a plummet of known volume when immersed in the liquid; (3) hydrometer method based on the volume displaced by a float of known weight; and (4) submerged float method based upon the submerged equilibrium, *i.e.*, floating of a bulb of known density.

For the petroleum industry in the United States, the definition of specific gravity and A.P.I. is as follows: The specific gravity of a petroleum oil and of mixtures of petroleum products with other substances is the ratio of the weight of a given volume of the material at a temperature of 60° F (15.56° C) to the weight of an equal volume of distilled water at the same temperature, both weights being corrected for the buoyancy of air. In Circular 57 of the U. S. Bureau of Standards is described the method of reading a hydrometer. A hydrometer made of glass consists of three parts. The upper part, or a graduated scale on which readings are taken, the enlargement of the tube containing mercury to weight the tube. The scale is graduated to read directly in specific gravity or Beaumé gravity. The relation of specific gravity readings to those of the Beaumé scale is given by the following formula*

$$\text{Specific gravity at } 60^{\circ} \text{ F} = \frac{140^{\circ}}{130^{\circ} + \text{Baumé reading}}$$

$$\text{Baumé gravity} = \frac{140^{\circ}}{\text{Specific gravity at } 60^{\circ} \text{ F}} - 130$$

To obtain the specific gravity of solids, Young's gravitometer may be used. It reads directly in specific gravity without calculation and the

* Scale adopted by the U. S. Bureau of Standards, Circular No. 57.

scale is graduated from 0.85 to 10.0. Young's gravitometer may also be used to obtain the specific gravity of liquids. The specific gravities are on a direct-reading scale.

Molecular Weight

The molecular weight of petroleum and its products, depending upon the origin, gives variations within broad limits. The determination of the molecular weight of lubricating oils is rather significant, since a lubricating oil with greater molecular weight appears more valuable than an equally viscous oil with a smaller molecular weight. V. Dallwitz-Wegner²³ established an equation for the wetting power into which the molecular weight enters, and arrived at the conclusion that the greater the molecular weight of an oil, the greater is its lubricating ability. Vogel¹²⁰ also ascertained that an oil has a flatter viscosity curve the larger its molecules, and that in the choice of two oils the one with a flat viscosity curve is a better lubricant.

The specific weight of various petroleum oils depends on their origin. The densities of American petroleum oils are the lowest; those of Russia, the highest. Commercially, it is of importance that petroleum oils from all sources have approximately the same density. The determination of density is made by means of a suitable hydrometer. Determinations of specific gravity and API gravity are made, using the U. S. Bureau of Standards and A.S.T.M. gravity correction tables.

Refractive Index

Refractometry is frequently used for the estimation of petroleum products. The Zeiss-Pulfrich refractometer or Abbé refractometer are used. The refractive index of solid paraffins indicates whether the original substance was ozokerite or paraffin or a mixture of the two. When tested at 90°, ozokerite shows a refractive index below 15.0, whereas the solid paraffins derived from petroleum will have $n = 15-30$ (Smelkus¹⁰⁹ and Holde and Schünemann⁵⁹).

When tested in the solid state, commercial paraffin waxes have a refractive index ranging from 1500-1540 at 30-130° F.⁸⁶ The specific dispersion $\Delta n/d$, where Δn is the difference between the refractive indices κ and κ_1 , and D the density at the same temperature, is constant within each class of hydrocarbons, but may be used to distinguish between saturated, unsaturated, and aromatic hydrocarbons. In case of unsaturated bonds, the specific dispersion grows with the number of double bonds.

Darmois found²⁴ for saturated aliphatic and saturated cyclic hydrocarbons $n = 155$; for unsaturated cyclic and unsaturated aliphatic with one double bond, $n = 190$; and for unsaturated aliphatic hydrocarbons with two double bonds, $n = 225-230$.

Le Roy,¹⁰⁰ using a Zeiss-Abbé refractometer at a temperature of 15°, found the following values:

Table 9

	Refractive Index
American oils:	
crude	1.4540
petroleum spirit (sp. gr. 0.720)	1.3995
white burning oil	1.4430
Russian oils:	
crude	1.4595
petroleum spirit (sp. gr. 0.720)	1.4105
white burning oil	1.4530
Roumanian oils:	
crude	1.4639
petroleum spirit (sp. gr. 0.720)	1.4055
white burning oil	1.4560

Oil Tests

Determination of Color Values

The color values of oils may serve to check correct processing in refining. The color values of oils are determined by comparison in a tintometer with standard chromate solutions or colored glasses. In the Lovibond tintometer used in the United States, the color values are given

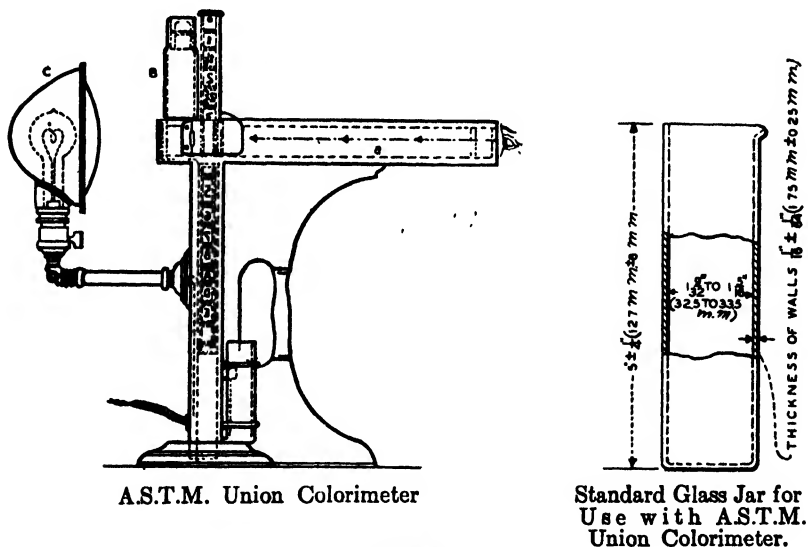


FIG. 34.

for oil cells of different length, the short cells being used for dark oils and long cells for light-colored oils. Violet tints indicate paraffin-base crudes. Oils of low viscosity usually show light colors. Colorimeters are instruments designed for color determination. The ASTM Union Colorimeter (Union Petroleum Company, Philadelphia) is used for determining the color of engine, machinery, and cylinder oils by comparison with standard color glasses (Fig. 34). The oil to be tested is placed in a glass jar of given dimensions and placed in one of the circular compartments

of the colorimeter and in the opposite compartment is introduced a glass jar of the same dimensions filled with water-white gasoline or distilled water. Standard glasses are placed in the slot of the colorimeter and the slide is then closed. The color of the oil is then compared with the standard glass.

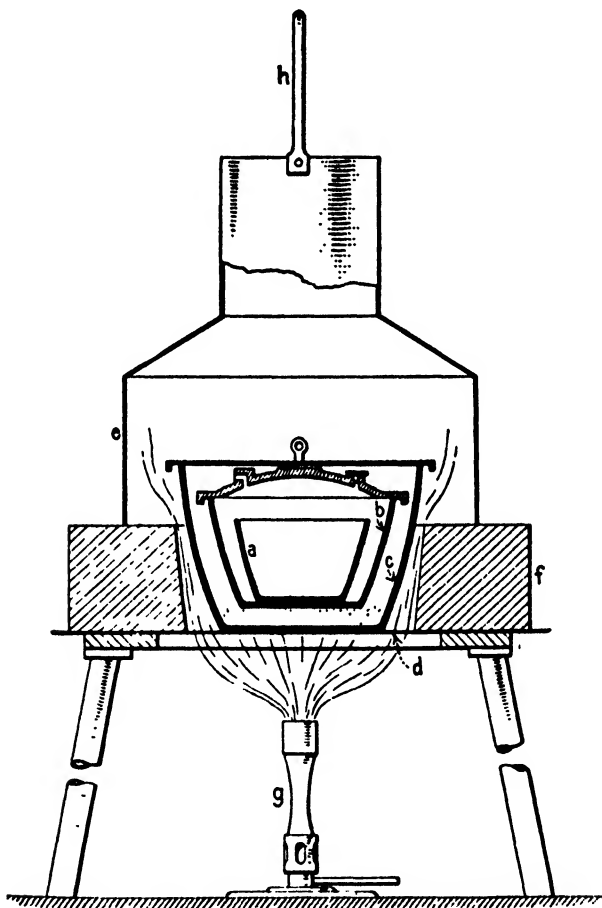


FIG. 35.

Carbon Residue Test

The kind of oil, as well as the type and condition of the engine in which it is used, determine the amount of carbon deposit. For instance, in lubrication processes, evaporation, cracking, and subsequent carbonization of traces of lubricating oil leaking past the piston rings into the cylinder head are not desirable, and an oil producing the least carbon deposit must be selected.

The oil sample is placed in a weighed porcelain crucible which is contained in a larger Skidmore cast-iron crucible with lid and air vent. The latter crucible is placed in a large sheet-iron crucible supported on a tripod and surrounded by a shield and chimney. A Meker burner heats the apparatus and smoking is observed in approximately 10 minutes.

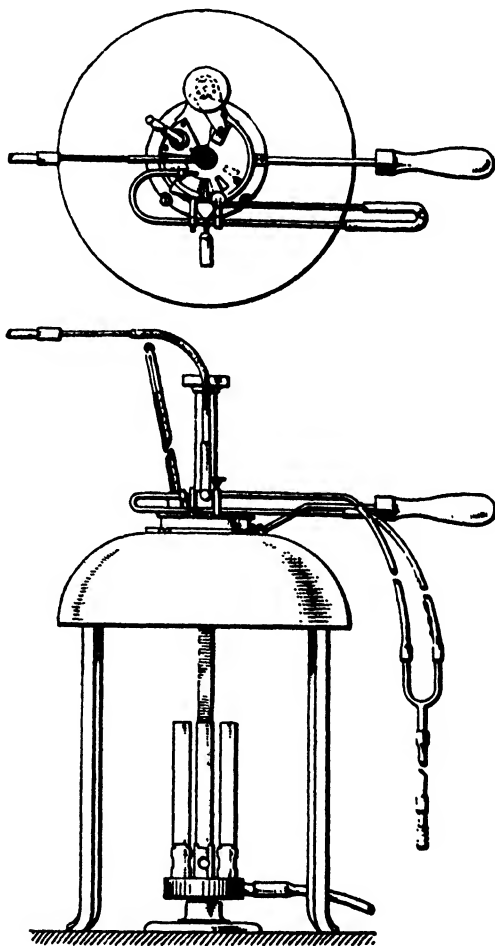


FIG. 36.

A.S.T.M. Standard
Pensky - Mar-
tens Tester.

The oil vapors are ignited and afterwards burned for 63 minutes. The residue is weighed, after finally heating for 7 minutes, and the percentage of carbon residue is obtained. The residue may be subsequently ignited for the determination of the ash content of the oil (Fig. 35).

Flash-point Determination

Although the flash-point test for oils is not a definite criterion of the spontaneous ignition temperature (an oil of high flash point indicates

only to a certain extent a good resistance to spontaneous ignition and explosion, for instance, in the lubrication of air compressors), it is of some value, as there is a relation between the flash point and the nature of the original crude oil and manner of refining of the oil. There is an increase in the flash point for fractions from the same crude with rise in boiling range, specific gravity, and viscosity. The flash point is related to the volatility of the oil.

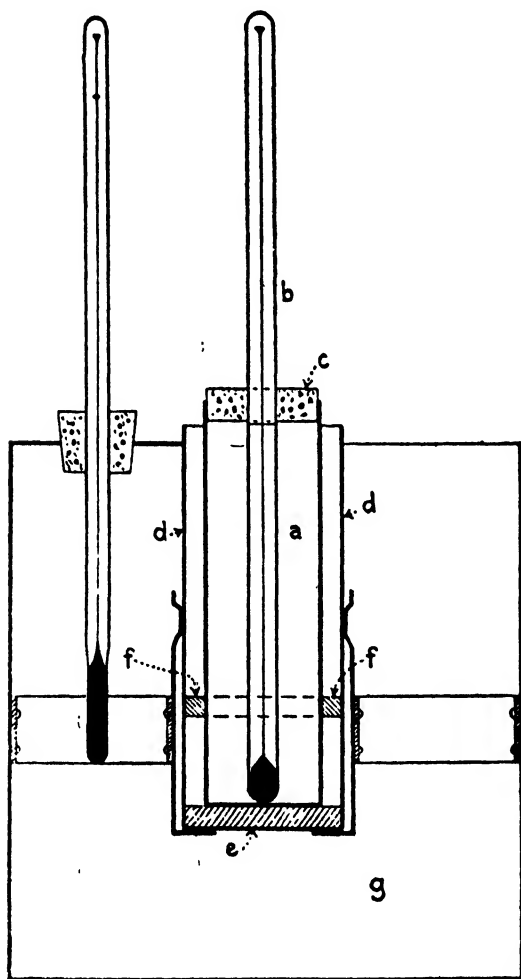


FIG. 37.

The Pensky-Martens tester, ASTM Designation D-93-22 (Fig. 36), consists of an oil cup supported in a cast-iron bath. The oil-cup cover is fitted with a thermometer, a stirrer, and a shutter device. The temperature is raised at the rate of 10°F per minute; the test flame is

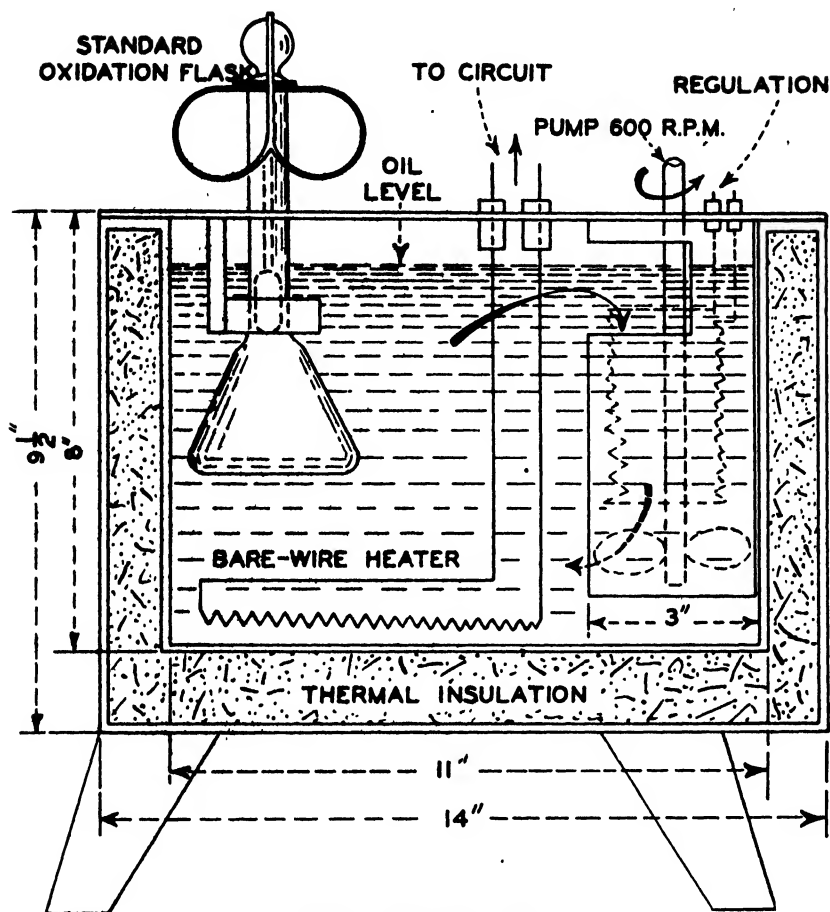


FIG. 38. Oxidation Bath.

applied every 2° below 220° F, and every 5° above this temperature. For testing lubricants, the open flash point is considered more reliable than the closed method. The Pensky-Martens apparatus standardized under IPT Serial Designation L.O. has the oil cup cover replaced by a simple clip carrying thermometer and test flame. The temperature is raised 10° F per minute, or until a flash appears on the surface of the oil (open flash), and then until the oil vapors burn for 5 seconds (ignition point).

Determination of Cloud- and Pour Point

The cloud-point test in dry dark oils indicates the temperature at which formation of wax crystals takes place. Verver¹¹⁹ discussed methods used in the determination of cloud points. The lowest temperature at which the oil flows under a small stress, produced by tilting the container of the oil, is the pour point. The test-jar surrounded by an air

jacket must be maintained at a temperature close to the pour point of the particular sample and is examined every 5°F until no movement of oil is shown when held horizontal for 5 seconds. The temperature 5°F above this corresponds to the pour point (Fig. 37).

Oxidation Test

The oxidation number of lubricating oils is determined by the Sligh oxidation test (Proceedings ASTM, Vol. 27, p. 461, Part 1 (1927)). The apparatus (Figs. 38, 39) is composed of a conical oxidation flask

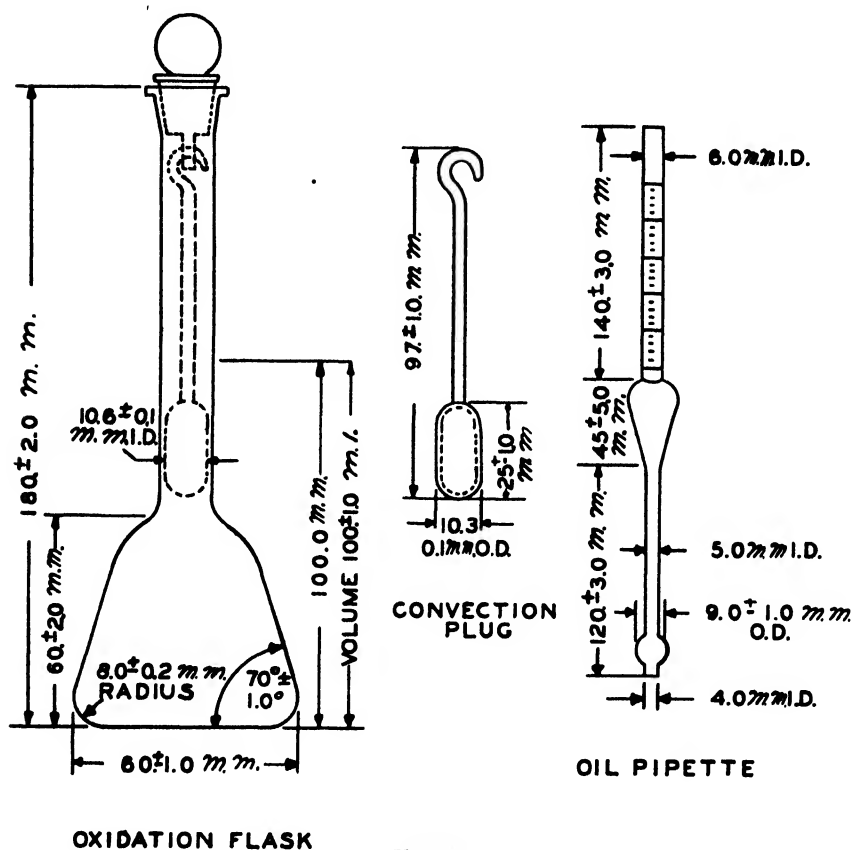


FIG. 39.

and an oxidation bath. A sample of 10 grams of oil in a stoppered flask, of a design indicated on the figure, from which air is displaced by oxygen, is maintained at 200° in an oil bath for 2.5 hours. The number of milligrams of asphaltenes formed, determined by dissolving the oil in petroleum ether and filtering through a Gooch crucible is termed the "oxidation number" of the oil.

The oxidation test is of importance because in steam engines and

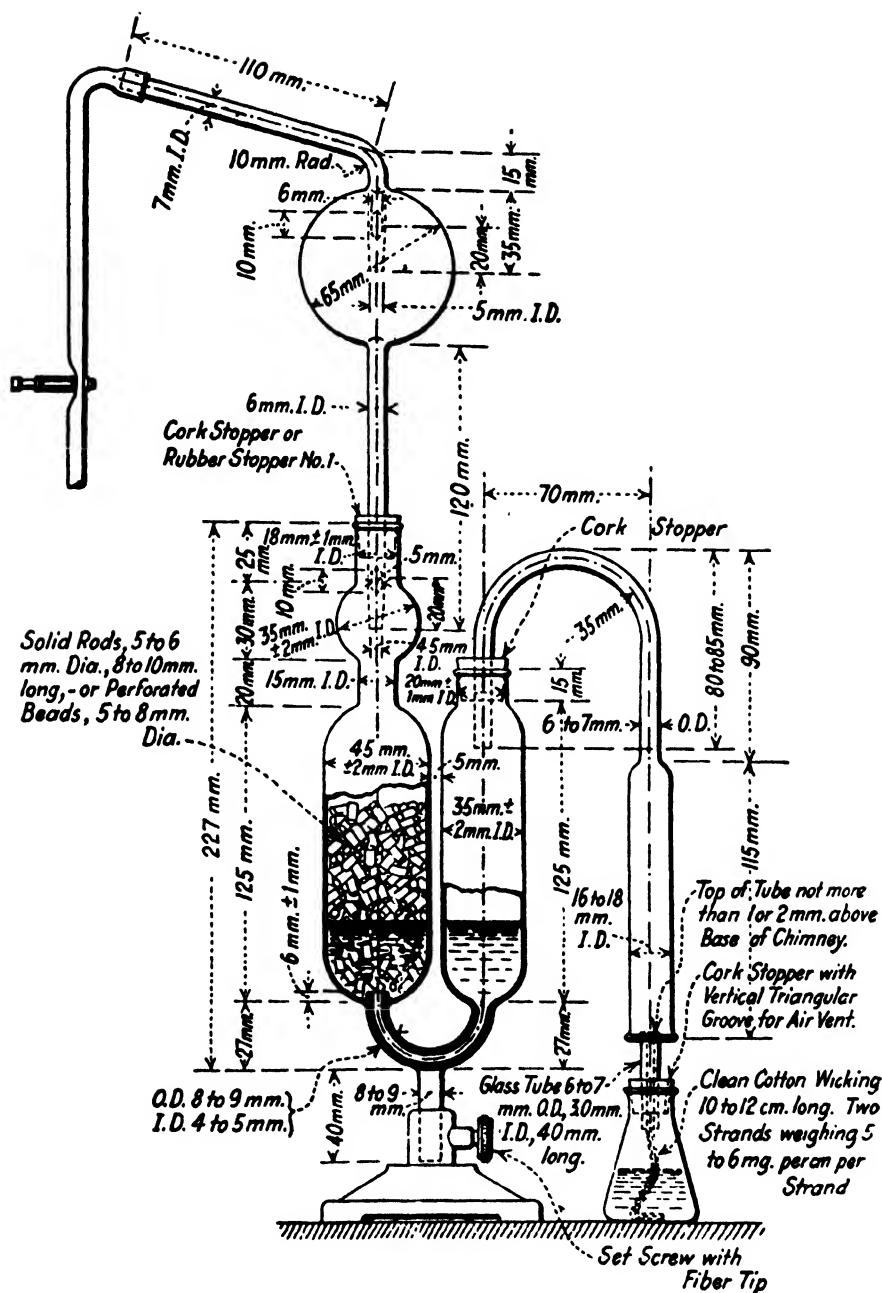


FIG. 40. Apparatus for Determining Sulfur in Oils.

steam turbines lubricating oil may be subjected to high temperatures in the presence of air, which causes oxidation of the oil resulting in the formation of corrosive acids, as well as in the deposition of sludge, which may interfere with lubrication. The oxidation factor in steam-turbine lubrication is especially detrimental where the lubricant must have a high degree of demulsification.

Sulfur Determination

Sulfur in lubricating oils may be determined by the lamp method, ASTM D 90-34T, presented on the figure, or by the bomb method, ASTM D 129-34. Which of these two methods is applicable depends upon whether or not the oil can be burned completely in a wick lamp. The first method is used for the determination of sulfur in oil which can be burned completely in a wick lamp. The apparatus as shown in the figure consists of an absorber of chemically-resistant glass, a chimney connected with the absorber by a cork stopper, a spray trap connected with the absorber also by a cork stopper, and a small lamp consisting of an Erlenmeyer flask with a wick tube projected above the cork entering the flask. A filter pump supplies continuous suction. For the test, about 15 ml of oil are poured into the dry lamp, and 10 ml of sodium carbonate solution diluted with 10 ml of distilled water are put in the absorber. The chimney and spray trap are rinsed with distilled water. Gentle suction is applied to both absorbers; the oil and alcohol lamp are lighted, and placed under the chimneys. The suction is adjusted so that a steady flame 12-18 mm in height is obtained. The sulfur content of the oil is calculated from the following formula:

$$\text{Percentage of sulfur} = \frac{\text{Ml of HCl for blank} - \text{Ml of HCl for sample}}{\text{Grams of oil burned} \times 10}$$

The bomb method, ASTM D129-34, is rapid and accurate. The sample (0.6-0.89) is weighed into the sample container, placed in position, 20 ml of water added to the bomb, and the latter tightly closed. The bomb capacity is 300-500 ml and is made of high nickel-chromium alloys. Oxygen is slowly admitted up to a pressure of 25-40 atmospheres. After firing and standing 10 minutes, the residual oxygen is released and the content of the bomb washed into a beaker. After filtering into a 250-ml beaker, 2 ml of concentrated hydrochloric acid and 10 ml of saturated barium chloride solution (10-per cent) are added from a fine-tipped pipette to the boiling solution while stirring. After boiling for 5 minutes, it is allowed to stand hot 1 hour, filtered, and washed until washings are free from chloride. Ignited and weighed, the percentage of sulfur is determined from the formula:

$$\% S = \frac{\text{Grams of BaSO}_4 \times 13.734}{\text{Grams of oil used}}$$

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Briggs and Schmidt, 29, 97, 163, 164, 180
 Briggs, Du Cassé and Clarke, 32
 Bright, 355
 Brillouin, 18
 Brinjes, 208
 British Celanese, Ltd., 463
 Broadbent, 377
 Brodersen, 192, 196
 Broughton and Squires, 22
 Brooks and Bacon, 1, 52
 Brooks and Humphrey, 404
 Brown, 6, 266, 294, 458, 494, 499
 Brown and Lum, 176
 Browner, 203
 Brownlee and de Ganahl, 383
 Brune, 627
 Brunnbauer, 369
 Bryan, 459
 Buc, 233
 Buchner, 177
 Bühling (Apparatus Construction Co.), 268
 Bukh, 291, 292, 311
 Bukh and Mirzoeva, 310
 Bukh, Pivovarova and Mirzoeva, 310, 311
 Bull, 515
 Bullock, 201
 Bunge, 171
 Burck, 237
 Bureau of Mines, 219, 461
 Burek, 266
 Burkby, 185
 Burton, 42, 43, 44, 53
 Burwell (Alox Chemical Corporation), 290, 324
 Buschmakin, 11, 33, 36
 Buschman, 192
 Buttho, 468
 Butler, 207
 Bututect, Inc., 411

C

Cage, J. M., 347, 348
 Calanter, 168, 170, 275
 Caldwell, 69
 Cameron, 28, 29, 74, 237, 238, 249, 253
 Camp (de), 251
 Campbell, 295
 Canadian Industries, Ltd. (Banbury and Clark), 174
 Canals and Mousseron, 15
 Cannon, 326
 Canton, 456
 Caroselli, 439, 440
 Caroselli and Heins, 409
 Carpsow, 428
 Carr, 241, 242
 Carrier, 480
 Carroll, 228
 Carver, 137, 494
 Cassé (du), 32
 Cassel, 100, 101
 Cavalli and Ostorero, 440
 Cerf (L. B. Smith), 370
 Cew (de), 197, 404
 Chader, 424
 Chaffin, 200
 Chafneux, 447
 Chamberlain, 165
 Chambige, 416
 Chamot, 475
 Champion, 420
 Chanut, 185
 Chapman, 198
 Chappel, 428
 Charitschkoff, 78, 526, 540, 544
 Charlotte, 200
 Cheesman and King, 68, 69
 Chemische Fabrik vorm. Griesheim-Electron, 203

Chemische Fabrik vorm. Pott G.m.b.H. (Müller), 193, 196
 Chemische Fabrik vorm. Sandow, 181, 184, 190, 191, 193, 194
 Chemische Fabrik vorm. Wiernick A.-G., 173
 Chemische Fabrik vorm. Westend, 172
 Chemische Forschungsgesellschaft m.b.H., 196
 Chemische Seifenfabrik vorm. K. Baumheier A.-G., 174
 Cheng, 498
 Child, 20, 21, 171
 Christiansen, 185
 Christman, 462
 Chwala, 195, 200
 Chwala and Waldmann, 195
 Clark, 93, 95, 98, 174, 455, 460
 Clark and Mann, 19, 20, 28, 29, 74
 Clark, Sterrett and Lincoln, 455
 Clarke, 32
 Clarkson (Du Pont Co.), 233
 Clason, 326
 Clausius-Mosotti, 47
 Clavel, 253, 384
 Clayton, 24, 33, 153, 161, 162, 163, 166, 373, 406, 531
 Claytor, 309
 Clifford, 546, 547, 548
 Cloez, 525
 Cloud, 263, 282
 Cloves, 61, 62, 63, 64, 71, 74
 Cockbain, 65, 101, 168
 Coehn, 40, 41
 Coggeshall and Reilly, 310
 Colas Products, Ltd. (Terry, Gabriel and Blotte), 410
 Colbeth (Baker Castor Oil Co.), 320, 321, 322
 Cole, 293
 Collier, 176
 Colloidal Equipment Corporation (Cunniff), 206
 Compagnie Général d'Exploitation des Brevets et Procédés de Recuperation Bregat Société, 299
 Compagnie Industrielle et Minière du Nord et des Alpes, 420
 Compagnie National de Matières Colorantes et Manufacture de Produits Chimiques du Nord Réunis, 190, 191
 Connell, 547
 Conradson, 460, 523
 Continental Oil Co. (Van Arken Mills), 325
 Conway, 236, 337
 Coombs, 399
 Cottrell, 336, 338, 341, 342, 348, 370
 Coudres (de), 125
 Court and Kasser, 178
 Craig, 461
 Cremac Marketing Co., Ltd. (L. S. Richards and E. M. Richards), 204
 Crockett and Oesper, 32
 Crosby, 296
 Cross, 294
 Cross (Cross Development Co.), 285
 Crown Rock Co., 408
 Cunniff, 206
 Curran, 260
 Curtin, 324

D

Dahlberg, 436
 Dahlstrum, 269
 Daimler, 192, 409

Dallwitz-Wegner, 451, 452, 453, 552
 Damany, M., 457
 Dameron, 346
 Dansk Gondalite A./S., 428
 Darnois, 552
 Daughdrill, 235, 257
 Davey, 40, 167, 202
 Davidson, 247
 Davies, 6, 93, 95, 98
 Davis, E. L., 325
 Dawson, 494
 Dayson, 276
 Dean, 540, 542
 Dean and Stark, 539, 541
 Debaecker, 257
 Debye, 520
 Debye and Hückel, 43, 515
 Decavel and Roegiers, 462
 Dede, 80, 134, 176, 254, 309
 Dehn, 412
 Dehydrators, Inc. (J. M. Cago), 347, 348
 Deiglmayr, 175
 De Laval, 372, 377
 Delco Co. (Waleh), 174
 Delft University, 403
 Delieu, 504
 Dellman, H., 295
 Demant, 380
 Dempster, 257
 Dennhardt, 297
 Descamps, 456
 Deutsch, 253
 Deutsche Erdöl A.-G., 179, 464
 Deutsche Hydrierwerke A.-G., 174, 182, 183, 193
 Deutsche Vialite Gesellschaft m.b.H., 426
 Devaux, 455
 Dillon (Union Oil Co. of California), 354
 Dimmig, 459
 Disney, 420
 Disney and Kernot, 178
 Distillers Company, Ltd. (Langwell), 172
 Ditterdorf, 294, 337
 Dijkshoom, 349
 Dodd, 55, 137, 272, 274, 431
 Dodge, 257
 Dogadkin and Lawrenenko, 197
 Donnan, 37, 48, 52, 53, 124, 133, 137, 502, 503
 Donnan and Barker, 71
 Donnan and Potts, 5, 6, 28
 Donny, 224, 225
 Dons, 292
 Doubleday, 454
 Dougherty, 534
 Douillet, 256
 Douthoff, 419
 Dow, 168, 528, 529
 Dow Chemical Co. (Grebe), 326
 Downing, 440
 Draper, 30, 57, 58, 81, 85, 96, 97
 Dreyfus, 193
 Duckham (Thermal Industrial and Chemical Research Co.), 251
 Duffing, 452, 453
 Dufour, 224, 225
 Duncan, 467
 Dunham, 63
 Dynatan, 381, 385, 404
 Dynatan and Thole, 1, 456
 Du Pont, 185, 233, 299, 373
 Du Pont (Gabelman and Henke), 192
 Du Pont (Lehner and Mentzer), 186, 196
 Dupré, 115, 126
 Dusssek Bitumen and Taroleum Co., Ltd. (Hatt), 206

Dussek Bitumen and Taroleum Co., Ltd. (Hatt, Harper and Mew), 419
Dvorkovics, 246
Dyer, 238, 250
Dyer and Heise, 267, 335, 337

E

Ebaugh, 324
Ebberts, 408, 412
Ebers, 532, 534, 535
Eckelman, 192
Edelman, 26
Eddy, H. C., 294, 332, 337, 340, 346, 349, 351, 352, 365, 368, 370
Eddy and Kiech, 349
Edeleanu, 381
Edmed and Newington, 322
Edwards, 264, 494
Egloff, 147, 462
Egloff and Benner (Universal Oil Products Co.), 267, 328
Egloff and Berkman, S., 228
Egloff, Nelson, Maxutov and Wirth, 334
Einstein, 17, 18, 99
Eisale, 182
Eitner, 451
Electro-Chemical Engineering Co. (Genderson), 233
Elisaffoff, 45
Ellis, 40, 43, 45, 46, 50, 51, 54, 78, 79
Elosegui, 408, 412
Elsenbast and Horine, 385
Empson, 203, 205, 378
Emulgia Vertriebsgesellschaft für Asphalt, Teer und Strassenprodukte [Clauser and Co. (Austria)], 420
Engelstat, 179
Engler, 525, 527
English, 173
Erfurt, 237
Erlich, 323
Erman, 187
Ermolenko and Guterman, 175
Ernotte, 414
Esterer, 257
Ettel, 518
Evans, 32, 254, 457
Evans and George, 137
Evers and Schmidt, 459

F

Fahl, 257
Fahrenwald, 408
Fain and Snell, 396, 426
Fair, W. F., Jr., 418, 421, 423
Fanto and Shitar, 347
Fanto and Spriter, 22
Faraday, 224
Farben - Gerbstoff Werke (Fleish), 191
Farbwerke vorm. Meister Lucius Brüning, 462
Faure, 315, 319
Fearis, 250
Feldman, 126
Feldmann, 17
Femme, 524
Ferguson and Dawson, 494
Ferns, Stapley and Harrison, 205
Ferri, 420
Ferrier, 67
Fette, 207
Findley, 171
Finkle, Draper and Hildebrand, 30, 57, 68, 81, 85, 96, 97
Firmini, 416
Fischer, M. H., 30, 31, 32, 33, 84

Fish, 201
Fisher, H. F. (Petroleum Rectifying Co.), 292, 294, 350, 354, 371
Fisher, E. and Harkins, 54, 85, 89
Fisher and Reddish (Kontol Co.), 309, 323
Flavigny, 405, 406, 419, 420
Fleck, 398
Fleckenstein, 244
Fleeger and Osborn, 337
Fleish, 191
Flett, 196
Flintkote Co., 176
Flintkote Co. (Gabriel and Blotte), 422
Flintkote Co. (Gregg), 210
Flintkote Co. (Gabriel, Blotte, Peard, Firmini, Meunier and van der Minne), 416
Flintkote Co. (Torrey, Gabriel and Blotte), 416
Flintkote Co. (Voerburg and Kirschbraun), 420
Ford, 458
Forbes, 280
Fortine, 235, 367, 475
Foster, 419
Foster Company (Foster and Seydel), 419
Fostiropol and Verona, 425
Foulk, 3
Foulon, 425
Fowler, 549
Fox, 410
Francis and Bennett, 446, 498
Frazer, 427
Frazer and Walsh, 204
Freedman, 197
Freeland, 254
Freeman and Schwab, 184
French, 364
Fresinski and Heusler, 195
Freud, 499
Freundlich, 16, 40, 46, 47, 117, 135, 138, 166, 454, 510
Freundlich and Elisaffoff, 45
Freundlich and Kroch, 162, 253
Freundlich and Loebmann, 253
Freundlich and Recklinghausen, 253
Freundlich and Rona, 45, 513
Freundlich and Sollner, 166
Friedel, 25
Friedman and Evans, 32
Friesenhahn, 190
Frumkin, 228
Frydender, 200
Fuchs, 320
Fuchs, F. E., 309
Fulton, 188, 189

G

Gabelman, 192
Gabriel, 399, 410, 416, 422
Gador, 411
Gail and Adams, 292
Galecki, 51
Ganahl, 383
Gand and Neal, 12
Gardner, 236
Garner, 450
Garrison (Petroleum Rectifying Co.), 350, 358
Garrison and van Loenen (Petroleum Rectifying Co.), 336, 351
Gas Fuel Corporation (Russell), 204, 210
Gas Light and Coke Co. (Murdock and Shannon), 202
Gause, 82
Gawalowsky, 384

Gehrke, 250
Geigy A.-G., 421
Geissler and Kleinert, 439
Gemant, 348
Genderson, 233
General Petroleum Corporation (Roth), 323
George, 137
Gerlach, 349
Gesellschaft für Chemische Industrie (Basel), 180, 193
Gesellschaft für Teerverwertung m.b.H. (Kraft), 418
Gewerkschaft Neue Erdöl Raffinerie Nerag, 427
Gibbs, 3, 5, 28, 61, 71, 72, 76, 77, 83, 100, 101, 122, 123, 124, 128, 129, 137, 141, 142, 146, 149, 150
Gibbs, 471
Gilbert, 228, 227
Gilpin and Schneeberger, 336, 338, 384
Girvin, 350
Glaser, 544
Ghadden Co. (Small), 417
Glossop, Bradley and Wilisdon, 250
Glover, 429
Glucksman, 178
Glyco Products Co., 187
Gnadagni, 420
Gnadagni and Bezso, 422
Goldthwait, 183
Goodwin, 174, 177, 208
Gordon, 31
Gortner, 40, 509
Gould, 551
Goutal, 254
Gouy, 42, 43, 47, 514
Graaf, 246, 275
Graefe, 540, 543, 546
Graefe and Fleck, 398
Graf, 182
Graham, 66
Gravenhagen, 349
Gray, 297, 385
Grebe, 326
Green and Ogden, 378
Green and Unthank, 258
Giegg, 210
Griffin, 85, 86, 87, 88, 99, 178
Grohn, 200
Groote (de), 287, 295, 297, 300, 301, 302, 303, 304, 305, 306, 307, 308, 309, 311, 312, 313, 314, 315, 316, 317, 318, 319, 321, 323, 325, 326, 327, 370, 530
Groote (de) and Adams, 301, 314
Gropengiesen, 204
Groschuff, 12, 23, 547, 548, 549
Gross and Engelstad, 179
Grotian, 19
Grover, 413
Grundlach, 174
Gruse, 379, 382, 526
Guggenheim, 83
Guglielmos, 456
Gulf Production Co. (Texas), 371
Gulf Publishing Co., 549
Gulf Research and Development Corporation (Ayres), 325
Gulf Research and Development Corporation (Hassler), 370
Günther, 193
Gurwitsch, 6, 28, 76, 77, 78, 81, 84, 155, 273, 275, 337, 338, 379, 384, 528
Guterman, 175
Gyement, 47

H

- Haber and Klemensiewicz, 136, 510
 Hackford, 457
 Hagen, 115
 Hahn, 525
 Haidberg, 438
 Hailwood, 174, 182, 183
 Hall, 24, 137, 532
 Hallas, 206
 Hallauer, 292
 Haller, 429, 605
 Halliburton Oil Well Cementing Co. (Clason), 326
 Halloran, 309
 Halvorsen, 415
 Halvorsen and Travis (Emulsion Products Corporation), 408, 409
 Hammond, 250
 Hanseatische Mühlenwerke A.-G., 173, 414
 Hanson (Petroleum Rectifying Co.), 347, 349
 Hardy, 90, 453, 454
 Hardy and Doubleday, 454
 Hargreaves, 203
 Harkins, 4, 13, 35, 53, 54, 57, 75, 85, 88, 89, 91, 92, 93, 94, 96, 97, 98, 126, 136, 137, 138, 140, 151, 446, 450, 456, 480, 488, 514
 Harkins and Beeman, 58, 85, 87, 96, 97, 99, 163
 Harkins and Brown, 494, 499
 Harkins and Feldman, 126
 Harkins and Freud, 499
 Harkins and Humphrey, 501, 502
 Harkins and Keith, 58, 95, 97
 Harkins and Zollman, 6
 Harkins, Brown and Davies, 6
 Harkins, Davies and Clark, 93, 95, 98
 Harkins, Young and Cheng, 498
 Harper, 419
 Harris, 185
 Harris (Petroleum Rectifying Co.), 342, 343, 370
 Harrison, 205
 Harrison-Carter, Ltd. (May and Barradell), 207
 Hart, 232
 Hart and Co., Ltd., 177
 Hartridge and Peters, 11
 Harvey, 69, 254
 Hasenclever, 463
 Haslam and Trobich, 458
 Hassler, 370
 Hatechek, 10, 18, 38, 48, 67, 336, 337, 338
 Hatt, 206, 419
 Haulon, 254
 Haure, 456
 Hauschildt, 377
 Hauser, 503, 531
 Hausman, 397, 402
 Hawthorn, 471
 Haynes, Marx and Rozies, 378
 Hay, 196
 Hays, 239
 Headley, 408
 Hebings, 170
 Hebler, 200
 Hedenstrand, 227
 Heine Vierson Bros., 378
 Heinrich, 350
 Heins, 409
 Heise, 267, 335, 337
 Heithecker, 250, 262
 Heitmann, 163, 462
 Hell and Midinger, 527
 Helmholtz, 42, 44, 52, 53, 514
 Helmholtz and Piotrowsky, 141
 Hemmer, 61
 Hendrey and Erbaugh, 324
 Henke, 192
 Henkel and Co. G.m.b.H., 195
 Henneberthe and Goutal, 254
 Henri, 54
 Henry, 115
 Henry and Sullivan, 277
 Hepburn, 414
 Herbsman, 293, 312, 372
 Herbsman (Industrial Products, Ltd.), 296
 Hercules Glue Co. (Lindstaedt), 180
 Hering, 237
 Herr, 287, 384
 Herrmann and Roehner, 463
 Herschel, 164, 523
 Herseman, 330
 Herseman (Petro Chemical Co.), 292, 295, 330
 Hessler, 385
 Heusler, 195
 Hewes, 428
 Hey, 179, 308
 Heyden von Typke, 8
 Higgins, 254
 Hildebrand, 28, 81
 Hildebrand and Lundell, 534
 Hildebrandt, 202
 Hill, 418
 Hillyer, 15, 23
 Hinrichs, 302, 382
 Hiss, 134
 Hite, 409
 Hittorf, 517
 Höber, 16, 27
 Höfer, 527
 Hofmann, 19, 29
 Hofmeister, 271
 Hoffman, 125, 164
 Hoffman and Marcusson, 540
 Hoffmann, 134
 Holde, 1
 Holde and Schünemann, 552
 Holde and Singalowsky, 450
 Holford and Harvey, 254
 Holmes, 28, 30, 475
 Holmes and Cameron, 28, 29, 74
 Holmes and Child, 20, 21, 171
 Holmes and Williams, 10, 28, 30, 75, 168, 171, 172, 198
 Holsten, 193
 Hopkins, 238, 255
 Horine, 385
 Hotlyn, 458
 Hough, 115
 Howes, 462
 Hubmajer, 174
 Hückel, 43, 515
 Hughes, 463
 Hull Co., 171
 Humphrey, 404, 501, 502
 Hunddiecker and Vogt, 183
 Hunter, 207, 237, 243, 244, 248
 Huntington, 263
 Hunziker, 412
 Hurdelbrink, 255
 Hurrell, 200, 203, 204, 206
 Hurrell and Co., Ltd., 204
 Hurst, 237
 Hutchings, 209
 Hutton and Fulton, 188, 189
 Hütz, 382
 Hützenlaub (P. Lechler Co.), 414
 Hyman, 296
- I
- I. G. Farbenindustrie A.-G., 169, 178, 179, 181, 182, 183, 184, 186, 188, 189, 190, 191, 192, 194, 291, 410, 411, 416, 462
 I. G. Farbenindustrie A.-G. (Beller and Luther), 182
 I. G. Farbenindustrie A.-G. (Beller and Pfaff), 185
 I. G. Farbenindustrie A.-G. (Daimler), 409
 I. G. Farbenindustrie A.-G. (Daimler and Thron), 409
 I. G. Farbenindustrie A.-G. (Eisole and Graf), 182
 I. G. Farbenindustrie A.-G. (Günther and Holsten), 193
 I. G. Farbenindustrie A.-G. (Klein), 417
 I. G. Farbenindustrie A.-G. (Luther), 193
 I. G. Farbenindustrie A.-G. (Luther and Beller), 182
 I. G. Farbenindustrie A.-G. (Marx and Brodersen), 196
 I. G. Farbenindustrie A.-G. (Marx, Brodersen and Bittner), 192
 I. G. Farbenindustrie A.-G. (Michel and Buschman), 192
 I. G. Farbenindustrie A.-G. (Pier and Christman), 462
 I. G. Farbenindustrie A.-G. (Steindorff, Daimler and Platz), 192
 I. G. Farbenindustrie A.-G. (Steindorff, Platz and Eckelman), 192
 Ihrig, 252, 277
 Iluin, 123, 328
 Illing and Kelly, 404
 Imperial Chemical Industries, Ltd., 174, 190
 Imperial Chemical Industries, Ltd. (Baldwin and Hailwood), 182
 Imperial Chemical Industries, Ltd. (Banbury and McGlynn), 182
 Imperial Chemical Industries, Ltd. (Hailwood and Todd), 183
 Imperial Chemical Industries, Ltd. (Hailwood, Shepherdson and Stewart), 174
 Imperial Chemical Industries, Ltd. (Howes), 462
 Imperial Chemical Industries, Ltd. (McGlynn and Todd), 191
 International Bitumen Emulsions Corporation, 412, 421, 422
 International Hydrogenation Patents Co., Ltd. (Birky), 463
 Ironsides Co., 463
- J
- Jackely, 402
 Jackson, 239
 Jacobs, 458, 544, 547
 Jaeger, 495
 James, 373
 Jamin, Amaury and Descamps, 456
 Javilier and Lavoloy, 534
 Jaworaki, 249
 Jayne, 540
 Jennings, 447
 Jensen, 266
 Jerie, 414
 Joel, 337
 Johansen, 187, 446
 Johnson, 301
 Johnson and Birger, 301
 Jones, 90, 170, 270, 342
 Joshi, 9, 36, 68, 98, 532

K

Kadmer, 174
 Kadt (de), 377, 403, 404
 Kahl, 171
 Kahler, 534
 Kalusowski, 29
 Kanook Co. Ltd., 209
 Kapatsinsky, 425
 Karpinsky, 253
 Kasser, 178
 Kauffmann, 238
 Keiser, 300, 302, 303, 304, 305, 306, 309, 311, 313, 315, 319, 321
 Keith, 58, 95, 97
 Kelley, 251, 253, 269
 Kelly, 404
 Kendrick, 13, 137
 Kenrick, 225, 226, 227
 Kenrick, Gilbert, and Wismer, 227
 Keppeler, Blankenstein and Borchers, 439
 Keynard, 173
 Kichalik, 232
 Kicke, 125
 Kiech, 249
 Killeffer, 377
 King, 65, 69, 209
 Kirschbraun, 173, 202, 408, 420
 Kirschbraun (Bennett Sons and Shears, Ltd.), 202
 Kirschbraun (Patent and Licensing Corporation), 418, 421
 Kissling, 458
 Kizber, 180
 Klein, 119, 209, 417
 Kleinert, 438, 439
 Klemensiewicz, 136, 510
 Kligerman, 292
 Kling, 264, 266
 Knaggs, 170, 174
 Knichalik, 147
 Kniga, 175
 Kniga and Wischniewskaja, 54
 Knopf, 172
 Knoss, 295, 337
 Knowing, 385
 Koch, 265
 Kothen, 454
 Koetschau, 299, 380
 Kohler, 179
 Kolbe, 528
 Königliche Stearinfabrik vorm Gonda, 177
 Kontol Co. (Ch. Fisher and Reddish), 323
 Kontol Co. (Meyers), 311
 Koppers, 232
 Kornilowa and Velynga, 325
 Kösters, 178
 Kraemer, 8, 59, 69, 96, 97, 98, 373, 456
 Kraft, 413
 Kraft-Phenix Cheese Corporation (Chapman), 198
 Kraft, 28
 Krannich, 179
 Krants and Gordon, 31
 Krebs, 227, 230
 Kremnev, 50, 166
 Kremnev and Papkowa-Kwitzel, 26
 Kresse, 406
 Kretzer, 412
 Kripke, 171
 Kroch, 162, 253, 347
 Kropffhammer, 185
 Krupenio, 234
 Kruyt, 329
 Kruyt and Edelman, 26
 Kubiarsky, 250
 Kuczynski, 197, 274, 304, 322, 339, 341, 370

Kurata, 462
 Kuznetzowa, 9

L

Labourse, 412, 427
 Lacan, 267
 La Farge and Chanut, 185
 Laird and Raney, 339, 347
 Lamb, 42, 44, 514
 Lamarle, 115
 Lancaster Processes, Inc. (Robinson), 198, 210
 Land (Petroleum Rectifying Co.), 348
 Landman, 244
 Lange, 78, 405
 Langham, 263
 Langmuir, 41, 42, 43, 75, 85, 86, 89, 90, 92, 95, 98, 126, 136, 137, 138, 139, 140, 151, 451, 453, 455, 514
 Langston, 461
 Langwell, 172
 Lapin, 17
 Laplace, 82, 115, 503
 Lapworth and Pearson, 30
 Lascaray, 8
 Lasche, 447
 Latimer-Goodwin Chemical Co. (Goodwin), 174
 Latzko, 406
 Laucks, 182
 Laval (de), 372
 Laval (de) Separator Co., 203, 207, 208, 377
 Lavoloy, 534
 Lawrenenko, 197
 Leary, 298
 Léauté, 432
 Lechler, 409, 410, 414, 420
 Lechler Co., 414
 Lechner, 456
 Lederer, 522
 Lehner, 186, 195
 Leidenfrost, 146
 Lembecke, 264
 Lenard, 135, 497, 498
 Lerch, 13, 277, 296
 Lesche, 253
 Levi, 429
 Levinstein, 29
 Levy, 171
 Lewis, 14, 24, 43, 44, 53, 54, 299, 300, 411
 Lewis, G. N., 122
 Liberthson, 415
 Lichtenecker, 49
 Lichtenstern, 414
 Liesegang, 10, 33
 Limburg, 9, 47, 51, 188, 312, 400
 Limburg (Patent and Licensing Corporation), 414, 433
 Lincoln, 455
 Linder and Picton, 40
 Lindner, 190, 192, 193
 Lindsay, 251
 Lindsley, 473
 Linstaedt, 180
 Lion Oil Refining Co., 332
 Lipatow, 17
 Lipatow and Lapin, 17
 Lipatow, Stepanowa and Feldmann, 17
 Lister, 417, 422
 Little and Sherman, 269
 Lodge, Oliver, 14
 Loebmann, 253
 Loesch, 173
 Lohnstein, 498
 Loomis, 166, 197
 Lorenz, 49
 Lorenzen, 265
 Lorents, 49

Lottermoser and Calanter, 168, 170, 275
 Low, 407
 Lozai, 256
 Luczak, 177
 Lum, 175
 Lundell, 534
 Lundsgaard, 186
 Luther, 182, 193
 Lyons, 99, 100

M

Maag, 188
 Mabery and Matthews, 446
 Mack, 398
 McArthur, 254
 McArthur and Maynard, 256
 McBain, 26, 41, 42, 85, 531
 McBain and Woo, 172
 McClave (Conservo Co.), 383
 McCongan and Hunter, 207
 McConanghay (Pre-Cote Corporation), 409, 415
 McConnell, 397
 McCoy, Shidel and Trager, 221
 McDonald (Petroleum Rectifying Co.), 347
 McElroy, 172, 187
 McFadden, 202
 McGivern, 177
 McGlynn, 182, 191
 McKesson, 422, 434, 437
 McKenzie, 837
 McKibben, 345, 368
 McLewis, 13, 449
 McMurray (M. and V. Tank Co.), 258
 McNear, 344
 Magnolia Petroleum Co., 368
 Magnus, 225, 227
 Mahone, 364
 Maksimovitch, 298
 Malamid, 180
 Malchow A.-G., 410
 Malette, 436
 Mandutz and Wohlleben, 249
 Mangelsdorff, 254
 Mangrove, 204
 Manley and Knoss (Texas Co.), 295, 337
 Mann, 19, 20, 28, 29, 74, 406
 Marangoni, 22, 115, 121
 Marcelin, 137, 455
 Marcet, 224, 242
 Marchant and Wells (J. P. Walker), 263
 Marcussou, 402, 434, 438, 540, 545
 Marden, 7, 22
 Markownikow, 527
 Markwood, 535
 Marshall, 13, 21, 78
 Martin, 448
 Marx, 192, 196, 250, 378
 Maschinenfabrik Augsburg-Nürnberg A.-G. (H. Dellmann), 295
 Maschinen - Apparaten Fabriken N. V., 267, 319
 Mason, 327
 Matheny, Langham, Cloud and Huntington, 263
 Mathieu, 437
 Matthews, 446, 534
 Matthews and Crosby, 298
 Matthews and Stamm, 12
 Matti, 188
 Maury, 11, 53
 Maxutov, 384
 May, 207
 May and Laird, 471
 Mayer, 174
 Mayer, Schaeffer, and Terroine, 27

Maynard, 256
 Mazetti, 349
 Mead and co-workers, 458
 Medwedkow and Sukhina, 430
 Menzer, 294
 Mendeleef, 525, 549
 Mensbrughe, 114, 115
 Mentzer, 186, 195
 Meredith (Petroleum Rectifying Co.), 265
 Merrill Co., 178, 180
 Meston, 258
 Metan Spolka, 403
 Metcalf, 22, 256
 Mette, 251
 Metz (de), 456
 Meunier, 416
 Meunier and Mathieu, 437
 Meunier and Maury, 11, 53
 Mew, 419
 Meyer, 147, 227, 232, 385
 Michael and Weiner, 309
 Michaelis, 42, 516
 Michaelis and Rona, 132
 Michel, 192
 Michell, 448
 Midingen, 527
 Miller, 157, 279
 Miller Combination Bailer and Pump Co. (Oklahoma), 263
 Millikan, 47
 Millikan and Sidwell, 471
 Millner, 43, 124
 Mirzoeva, 310, 311
 Miscall, 421
 Mizuta and Toda, 465
 Mohr, 533, 534
 Moissan, 549
 Mollering, 200
 Monson, 16, 288, 289, 293, 304, 312
 Montanwerke A. - G. (Ruebische), 180
 Montgomery, 408, 324
 Montgomery and Archibald, 427
 Monv, 383
 Mooney, 40, 43, 44
 Moore, 10, 80, 164, 473
 Moreton, 418
 Morgan, 81, 251, 411
 Morrell, 196, 295, 408, 464
 Morris, 156, 523
 Morway and Zimmer, 463
 Moscieki, 257, 274
 Moscieki and Kling, 264, 266
 Mossotti, 47, 115
 Mousseron, 15
 Mukherjee, 41
 Mulfarth, 137
 Müller, 193, 196, 206
 Mullin, 407
 Murdoch, 202
 Murex, 397
 Murphy, 170
 Murray and Patterson, 66
 Mushkin, 325
 Muszatti and Volterre, 458
 Muth, 339
 Myers, 413, 437, 438

N

Nagelstein, 68
 Narayanaswamy and Watson, 21
 Nasini and Rossi, 401, 433, 437
 Nasini, Rossi and Baliau, 483
 Nasini, Rossi and Santa, 12
 Naske, 200
 Nastjukoff, 381, 458
 National Aniline and Chemical Co., Inc. (Zwilmeyer), 210
 National Electric Light Association, 461

National Oil Products Co. (Wolfson), 233
 Nauman, 231
 Neal, 12
 Neill, 246
 Netzke (Bennett, Inc.), 414, 422
 Nellensteyn, 12, 397, 398, 400, 430, 431, 432
 Nellensteyn and Roodenburg, 401
 Nelson, 334
 Nelson, Hallauer and Dons, 292
 Nettel, 542
 Neubacker, 202
 Neubronner, 434, 437
 Neushabel Asphalt Co., Ltd., 411
 Newington, 322
 Newman, 38, 67, 69, 74, 163, 532
 Newton, 145
 Nichols, 59, 486
 Nishizawa, 125
 Nishizawa and Inoue, 182
 Noerdlinger (Chemische Fabrik Florsheim), 255
 Nohl, 174, 176, 188
 Nordlund, 163
 Nouy (du), 498
 Novak, 411
 Novotney and Hunter, 237
 Nugent, 11, 292, 531
 Nutley, 185
 Nuttall, 458
 Nutting, 155
 N. V. Chemische Fabrik vorm. Servo and Rosenbrock, 191
 N. V. Handel-Maatschappij "DeMa," 204
 Nyrop, 205

O

Oak, 440
 Oberlin, 326
 Oda, 184
 Odell and Thiele, 545, 546
 Oersted, 456
 Oesper, 32, 54
 Ogden, 378
 Ohse, 436
 Oil Reclaiming Co., 275
 Olwerke Stern Sonneborn, 462
 Oranienburger Chemische Fabrik A.-G., 194
 Oranienburger Chemische Fabrik A.-G. (Lindner and Russe), 190, 192
 Oranienburger Chemische Fabrik A.-G. (Lindner and Zickermann), 193
 Orelup, 184
 Osborn, 337, 440
 Ostorero, 440
 Ostwald, W., 17, 34, 35, 36, 38, 39, 275, 448
 Ostwald, Wo., 1, 100, 164
 Ostwald, Wo. and Siehr, 232
 Ostwald, Wo. and Steiner, 118
 Overgard, 417, 422, 423
 Owen, 90

P

Padgett, 27
 Page, 552
 Painter, Moreton and Hill, 418
 Paux and Co., 415
 Palmer, 254
 Pan-American Petroleum Co. (J. C. Black), 291
 Papkowa-Kwitzel, 26
 Parke, 267
 Parke and Graham, 66
 Paikhomenko, 197, 323
 Parks and Gibbs, 471
 Parsons and Wilson, 29, 38, 61, 62, 66
 Passavant Werke, 256
 Passler, 352, 369, 371
 Passler and Brunnbauer, 369
 Patent and Licensing Corporation (Braun), 423
 Patent and Licensing Corporation (Lumburg), 414, 433
 Patent and Licensing Corporation (Miscall), 421
 Patent and Licensing Corporation (Roediger), 415
 Patrick, 449
 Patterson, 66
 Paul, Allen and Rosengien, 204
 Pauli, 514
 Paulik, 231
 Pawlikowski, 340, 341
 Pavne, 324
 Peard, 416
 Pearson, 30
 Perrin, 57, 374, 437
 Perry and Bullock, 197
 Pester (Standard Oil Development Co.), 323
 Peters, 11
 Peterson, 256
 Petro Chemical Co., 292, 295, 330
 Petroleum Rectifying Co., 265, 295, 342, 343, 344, 346, 347, 348, 349, 350, 353, 358, 365
 Petroleum Rectifying Co. (Cnrg), 348
 Petroleum Rectifying Co. (Curr), 241, 342
 Petroleum Rectifying Co. (Cottrell), 370
 Petroleum Rectifying Co. (H. C. Eddy), 332, 340, 346, 349, 351, 352, 355, 369
 Petroleum Rectifying Co. (H. F. Fisher), 292, 294, 350, 354, 371
 Petroleum Rectifying Co. (Harris), 342, 343, 371
 Petroleum Rectifying Co. (McKibben), 345, 368
 Petroleum Rectifying Co. (McNear and Bowles), 344
 Petroleum Rectifying Co. (C. H. M. Roberts), 351, 353, 372
 Petroleum Rectifying Co. (Woolfin), 354, 355, 356, 369, 371
 Petroleum Sand Products Corporation, 198
 Petrov, 180, 188, 310, 383
 Pfaff, 185
 Philip, 446, 460, 461
 Pick, 523
 Pickara, 49, 50
 Pickering, 10, 20, 24, 25, 33, 34, 55, 56, 57, 79, 80, 84, 103, 133, 160, 161, 531
 Picton, 40
 Pier, 462
 Pilat, 195
 Pilat and Piotrowski, 264
 Pink, 256
 Piotrowsky, 141, 264
 Pippin, 255
 Pirbright Co., Ltd. (Beale), 256
 Pivovarov, 310, 311
 Planktonall Chemische Fabrik G.m.b.H. and Carpow, 428
 Plateau, 5, 18, 19, 114, 116, 121, 124, 129, 143, 144, 145, 146
 Platz, 192
 Plauson, 199
 Plauson (Mineral A.-G. Brig), 427
 Plauson's Forschungs Institut, 407, 440

Plauson's Forschungs Institut
(Stack), 426
Pletnjewa, 30
Podzus, 200
Poiseuille, 140
Polanyi and Bogdandy, 198
Pollak, 236, 269
Ponyatkov, 325
Poolman, 197
Popich, 463
Post (Luling Treating Plant),
239
Potts, 5, 6, 28
Pound, 11
Povey, 204
Povey and Hallas, 206
Powell, 305
Power Specialty Co., 265
Powis, 9, 46, 50, 51, 54
Prater, 377
Pravicha and Douillet, 256
Pre-Cote Corporation, 409, 415,
417, 428
Primrose, 264
Prutzmann, 147, 231, 250, 353,
541
Pure Oil Co. (Hvman and
Schlaudt), 296
Pure Oil Co. (Suthard), 320
Pushaj, 204
Putochowski and Strukowa, 531
Pyhala, 1, 302, 528

Q

Quineke, 5, 6, 115, 132
Quinby (Petroleum Rectifying
Co.), 347

R

Rabinerson and Kremnev, 50
Radulesco, 419
Ragowski, 166
Rakusin, 159, 528
Ralph, 278
Ramesohl and Schmidt, 205
Ramsden, 22, 73, 74, 79, 84, 121,
124, 130
Raney, 339, 347
Rasser, 177, 183
Raul, 297
Rayleigh (Lord), 22, 126, 134,
453, 496
Raynk, 258
Recklingshausen, 253
Redgrove, 454
Reddish, 309, 323
Redlich, 176
Rehbinder, 69
Reilly, 310
Reinders, 6, 7, 19, 125
Reinders and Hoffman, 125
Reiner, 432
Reiners, 80, 134, 176, 254, 309
Reistle, 159
Réné, 57
Renfrew, 267
Resinous Products and Chemi-
cal Co., 183
Reuss, 328
Reynolds, Tower and Lasche,
447
Richards, 197, 204
Richards and Carver, 494
Richards and Loomis, 166, 197
Richards and Stall, 456
Richardson, 21, 250, 393, 402,
403
Richardson and Griffin, 178
Richfield Oil Corporation
(Hewes and Chappel), 428
Rick, 409
Rickenbacher, 145
Rideal, 168, 227, 510
Riemann, 85, 87

Ries, 72, 73, 81
Riesen, 203
Riis, 436, 440
Riolland, 383
Rive (de la), 225
Robert and Frazer, 544
Roberts, C. H. M., 12, 44, 53,
56, 68, 85, 90, 153, 155, 162,
231, 283, 288, 289, 291, 299,
301, 303, 304, 313, 324, 351,
353, 367, 372, 377, 401, 446,
529
Roberts, C. H. M., and Smith,
171
Roberts, C. H. M., and Stenzel,
386
Roberts, C. H. M., Stenzel, and
Eberz, 532, 534, 535
Robertson, 37, 38, 61, 67, 298,
304, 532
Robeson, 187
Robinson, 157, 158, 293, 294, 325
Robinson and Sutherland, 417
Robinson (Blake-Smith), 292,
294
Robinson (Lancaster Processes,
Inc.), 198, 210
Rochner, 463
Rochow and Mason, 327
Roederer, 29, 415
Roediger (Patent Licensing
Corporation), 415, 422
Roegiers, 462
Rogers, 309, 311
Roginski, 163
Rona, 45, 132, 513
Ronheim, 448
Rouault, 412
Roodenburg, 401
Roos and Oesper, 32, 54
Roper, 521
Rose, 397
Rosengren, 204
Rosenthal, 267, 527
Rosetukow (Zentralnoe Biuro
Realizacii Isobretenija), 461
Rosewarke and Connell, 547
Ross, 200, 240, 262, 278, 401,
402
Ross, 12, 23, 401, 433, 437
Rost, 301
Roth, 323
Rothmund, 549
✓ Roy (Le), 552
Rozes, 378
✓ Russakow, Kuznetzowa and
Semenko, 9
Russe, 190, 192
Russell, 204, 210, 232, 465
Rutzerswerke A.-G., 246, 338,
382, 411
Rutzerswerke A.-G. (Kahl), 171
Ryzanovskii, 303

S

Sadakiyo, 370
Sadtler, 540
Sander, 256
✓ Sanval and Joshi, 36, 68, 98
Sansoute, 409
Scarlett, Morgan and Hilde-
brand, 81
Schaeffer, 27
Scheen and Kahler, 534
Schemyakin, 54
Schering and co-workers, 519
Schiff, 181
Schindler, 167
Schlaepfer, 10, 80, 176
Schlaudt, 296
Schmids Erben A.-G., 419
Schmidt, 28, 97, 163, 164, 180,
205, 233, 257, 301, 459
Schneeberger, 336, 338, 384
Schnobrich, 157
Schrader and Stahl, 203
Schrauth, 179
Schrödinger, 501
Schroeder, 201, 207, 257
Schroter, 519
Schulman and Cockbain, 65, 101,
168
Schulman and Rideal, 168
Schünemann, 552
Schütte, 198
Schwab, 184
Schwaiger and Sorensen, 519
Schwarz, 382
Scott, 428, 475
Seaman, Brnjes, and Goodwin
Ltd., 208
✓ Segal, 346
Segner, 115
Seibert and Brady, 342
Seifenfabrik A.-G. (Steinfels),
181
Seifritz, 10, 60, 69, 75, 76, 97,
98, 166, 170
Seitz and Lechner, 456
Seiler, 256
Selater and Stephenson, 473
✓ Sen, 47
Seng (Union Products Co.), 428
Senger, 539
Sepulchre, 256
Serrallach and Jones, 90
Serrallach, Jones, and Owen, 90
Seydel, 419
Sevffert, 231
Seymour, 251
Shannon, 202
Sharples, 374, 377, 464
Sharples Specialty Co., 297, 377,
378
Sharples Specialty Co. (Jones),
270
Shaw, 256
Shaw and Beale, 255, 337
Shea, 67, 158, 289, 291, 364
Shepherdson, 174
Sheppard, 29, 74, 163, 254
Sheppard and Sweet, 11
Sherman, 269
Sherrick, 31, 41, 78, 168, 271,
273, 274, 293, 398, 531
Sherrick and Jones, 342
Shidel, 221
Shitar, 347
Shorter, 48, 72, 122, 123, 124
Shropshire, 210
Sibree, 18
Sidwell, 471
Siehr, 232
Siemens and Schuckertwerke
A.-G., 350
Siemens and Schuckertwerke
A.-G. (Heinrich), 350
Silbereisen, 13
Silberstein, 49
Sinclair Refining Co. (Robert-
son), 298, 304
Sinclair Refining Co. (Shrop-
shire), 210
Singalowskv, 450
Singer (F. E. Fuchs), 309
Skalmowski, 432
Skinner, 382, 456
Sligh, 458
Slonim and Beklemischew, 345,
355
Small, 417
Smelkus, 521, 552
Smith, 7, 171, 248, 250, 258,
282, 381, 414, 425
Smith, E. L., 29
Smith, I. B., 371
Smith, R. C., 19
Smith and Douthoff (Barber
Asphalt Co.), 419

- Smith (Barber Asphalt Co.), 415, 421, 424
 Smith (Separator Corporation), 263
 Smoluchowski, 42, 44, 47, 51, 514
 Snell, 166, 396, 426
 Snyder, 458
 Sociedad Anonima Papeteries Navarre, 175
 Societa Anonima Permolio, 410
 Société Anonyme André Fils, 383
 Société Anonyme des Pétroles, Huilles et Derivés, 250, 383
 Société Chimique de la Route et Ponce, 411, 426
 Société des Produits Chimiques et Matières Colorantes de Mulhouse, 190
 Société Rol. Lister et Cie., 409
 Socony-Vacuum Oil Co., 420
 Söllner, 166
 Sörlner and Ragowski, 166
 Sorensen, 511, 519
 Sorge, 256
 Southagen, Wood and Kanook Co., Ltd., 209
 Southard, 461
 Southcombe, 445, 449, 450
 Spalteholz, 177, 541
 Sparks (Standard Oil Co. of Indiana), 413
 Speakman and Chamberlain, 165
 Specialty Sales Corporation, Ltd. (Bavin and Powell), 299
 Specialty Sales Corporation, Ltd. (Powell), 305
 Sperling, 257
 Spiegler, 253
 Spielmann, 430
 Spiers, 424
 Spilker, 147, 231
 Spriter, 22
 Squires, 32
 Seegal, 165
 Seelski, 544, 545
 Seemenko, 9
 Seyehra and Seegal, 165
 Stables and Wilson, 19
 Stack, 426
 Stahl, 203
 Stall, 456
 Stamm, 12
 Stamm and Kraemer, 69, 96, 97, 98
 Stamm and Svedberg, 57
 Standard Français de Pétroles, 432
 Standard I. G. Co. (Burkby and Nutley), 185
 Standard Oil Co. (Indiana) (Payne and Montgomery), 324
 Standard Oil Co., 292, 413
 Standard Oil Co. (McConnell), 397
 Standard Oil Co. (Rose), 397
 Standard Oil Co. (Steininger), 415
 Standard Oil Co. (Taylor), 413
 Standard Oil Development Co., 196, 309, 323, 397, 429, 465
 Standard Oil Development Co. (Buc), 233
 Standard Oil Development Co (Cannon), 326
 Stanolind Oil and Gas Co. (Bays), 258
 Stanzas, 51
 Stapley, 205
 Stark, 539, 541, 544
 Steager (Brown. Boveri Corporation), 458
 Steen, 209
 Steenberg, 210
 Stehr, 320
 Steik, 52
 Stein, 336
 Steiner, 118
 Steindorf, 192
 Steinfeld, 181
 Steininger (Standard Oil Co. of Indiana), 415, 417
 Steinits, 447, 464
 Steizer, 381
 Stenzel, 386, 532, 534, 535
 Stepanowa, 17
 Stephens, 257
 Stephenson, 473
 Stern, 43, 514
 Sterrett, 455
 Stewart, 174
 Stewart, Reisen and Hargreaves, 203
 Stokes, 18, 43, 373, 430
 Stoops, 521
 Strache and Glaser, 544
 Stratford (Texas Co.), 171
 Straw, 131
 Streppel, 404
 Strother, 265
 Strukowa, 531
 Stutler, 465
 Submarine Signal Co., Ltd., 198
 Sucabu, 402
 Suchowolskaja, 136
 Suchy and Luczak, 177
 Sugden, 98, 99, 494, 495
 Sukhina, 430
 Sullivan, 277
 Sultzew, 464
 Suman, 155
 Summerfield, 407
 Sumner, 163
 Sunder, 329
 Sun Oil Co. (Pew, Jr.), 404
 Suthard, 320
 Sutherland, 417, 461
 Svedberg, 59, 373
 Swartslander, 251
 Sweet, 11
 Szegvari, 25, 209
 Szidon, 197, 407, 409
 Szyzkowski, 120
- T**
- Tabary, 414, 429
 Taggart, 43, 135
 Talmud and Suchowolskaja, 136
 Tapping, 173
 Taranow and Twertzin, 299, 317
 Tartar, 63
 Tartar, Duncan, Shen, and Ferrier, 67
 Tate, 498
 Tatman, 236
 Taylor, 227, 413
 Teegen, 257
 Terroine, 27
 Terry, 410
 Terry and Craig, 461
 Terry, Gabriel, and Blotte, 399, 410, 422
 Testori, 539
 Texas Co., 171, 177
 Texas Co. (E. L. Davis), 325
 Texas Co. (Hendrey and Erbaugh), 324
 Texas Co. (Thurston), 190, 415
 Texas Pacific Coal and Oil Co. (Baker, Fleckenstein and Landman), 244
 Tfol, 171
 Thalman, D. E., 421
 Thermal Industrial and Chemical Research Co., Ltd., 251, 423
 Thermal Industrial and Chemical Research Co., Ltd. (Chader Spiers, and Arnold), 424
 Thiberge, 202
 Thiele, 545, 546
 Thole, 1, 456
 Thomas, 35, 81
 Thomson, 121, 137
 Thomson, W., 497
 Thomson-Houston Co., Ltd., 170
 Thompson, 221, 412, 421
 Thompson and McGivern, 177
 Thornley and Co. (Delaware), 407
 Thornley, Tapping, and Keynard, 173
 Thorpe, 464
 Thurston, 190, 415
 Tickell, 121
 Toda, 465
 Todd, 183, 191
 Tomasello, 423
 Torrey, 416
 Tower, 447
 Trager, 221
 Traube, 8, 119, 135, 494
 Traube and Kicke, 125
 Traube and Klein, 119
 Traube and Nishizawa, 125
 Travis, 199, 408, 409
 Traxler, 399
 Traxler and Coombs, 399
 Tretolite Co., 155, 220, 297, 300, 301, 309, 310, 312, 314
 Tretolite Co. (de Groote), 295, 300, 301, 303, 305, 306, 307, 308, 311, 312, 313, 315, 317, 318, 319, 321, 323, 325, 326, 327
 Tretolite Co. (de Groote and Keiser), 300, 302, 303, 304, 306, 309, 311, 313, 321
 Tretolite Co. (de Groote and Monson), 312
 Tretolite Co. (de Groote and C. H. M. Roberts), 303
 Tretolite Co. (de Groote and Wirtel), 312, 314, 315, 316
 Tretolite Co. (de Groote, Adams and Keiser), 305
 Tretolite Co. (de Groote, Adams, Keiser and Wirtel), 321
 Tretolite Co. (de Groote, Keiser and Wirtel), 300, 305, 309, 311, 313, 321
 Tretolite Co. (de Groote, Keiser, Faure and Wirtel), 315, 319
 Tretolite Co. (de Groote, Monson and Keiser), 304
 Tretolite Co. (de Groote, Monson and Wirtel), 312
 Tretolite Co. (de Groote, Wirtel and Keiser), 300
 Tretolite Co. (Oberlin), 326
 Tretolite Co. (Roberts, C. H. M.), 301, 303, 304, 313
 Tretolite Co. (Stehr), 320
 Tretolite Co. (J. Ch. Walker), 311
 Trillat, 453
 Trobich, 458
 Trumble, 337
 Tucker, 5, 365, 503, 531
 Turner, 258
 Twertzin, 299, 317
 Twine, 238
 Twitchell, 180, 182
 Twitchell Process Co., 189
 Tyler (Du Pont Co.), 299
- U**
- Ubbelohde, 450
 Uddeholms Aktiebolag (Mayer), 174

Uhele, 177
 Union Oil Co., 354
 Union Oil Co. (Bray), 428
 Union Oil Co. (Bray and Beckwith), 423, 433
 Union Oil Co. (Fishcr, H. F.), 354
 Union Oil Co. (Scott), 428
 Universal Oil Products Co. (Egloff), 462
 Unthank, 258
 Urban and White, 41, 514
 Uren, 155
 Usher, 42, 44, 52

V

Valentiner, 125
 Van Arken Mills, 325
 Van Calcar, 372
 Van Dedem (J. G. W. Baron), 287, 288
 Vandone, 439
 Van der Kolk, 480
 Van der Meulen and Riemann, 85, 87
 Van der Minne, 285, 416
 Van der Ploeg, 179
 Van der Waals, 57, 101, 227
 Van der Willigen, 145
 Van Loenen, 336, 351
 Van Loenen (Black-Smith Co.), 294, 349
 Van Westrum, 418
 Veith, 380
 Velynga, 325
 Vellinger, 504
 Vellinger and Delieu, 504
 Vellinger and Radulesco, 419
 Vereinigte Dachpappen A.-G. (A. Brautigam), 410
 Verona, 425
 Verona and Fostiropol, 424
 Verver, 558
 Verwey, 106, 430
 Vincent, 447
 Vischnevskaja and Kniga, 175
 Voerborg, 420
 Vogel, 552
 Vogt, 183
 Vorhard, 533, 534
 Volkmann, 494
 Volokh, 237
 Volterre, 458
 Von Ammag, 28
 Von Boyen (Montanwachsfabrik G.m.b.H.), 179

Von Weimarn, 199
 Vredenburg (Bendixen), 206

W

Wack, 292
 Wagner, 234, 250, 293
 Wailes-Dove Bitumastic, Ltd. and Shaw, 429
 Waldmann, 195
 Waldmann and Chwala, 195
 Walger, 464
 Walker, 293, 296, 311, 314
 Walker, J. P., 263
 Walsch, 174, 203, 204, 336
 Walther Verlag Verein Dachpappen Fabriken A.-G., 434
 Waterman, 404
 Watson, 21
 Watts, 421
 Wayne, 299, 319, 320
 Webb, 276
 Weber, 381, 432, 439
 Weber and Bechler, 439
 Weichherz, 80, 70, 71
 Weichherz and Pletnjewa, 30
 Weine, 309
 Wen, 270
 Weiss, 267, 434, 438
 Weiss and Vellinger, 504
 Wellman and Tartar, 63
 Wells, 263
 Wells and Southcombe, 445, 449, 450
 Werner, 210
 West and Dodd, 187
 Westenholz and Nyrop, 205
 Westinghouse Co., 378
 Whatmough, 169, 207
 Wischnevskaja, 54
 Whitcomb, 462
 White, 41, 255, 514
 White (Oil Separators, Ltd.), 258
 White and Marden, 7, 22
 Whitney and Straw, 131
 Wiegner, 55
 Wiener, 49
 Wiernick Co. A.-G., 178
 Wiggins, 224, 235
 Wikner, 236, 246
 Wilcox, 348
 Wilisdon, 250
 Wilharm, 454
 Wilke, 235, 250
 Wilkin, Oak and Barnard, 449

Williams, 10, 28, 30, 75, 168, 171, 172, 198, 239, 358, 368, 369
 Williams and Ironsides Co., 463
 Williams and Russell, 465
 Willows, 51
 Wilson, 19, 24, 29, 38, 60, 61, 62, 66, 137, 162, 184
 Wilson and Barnard, 450, 453, 454
 Wilson, R. E. and Ries, 72, 78, 84
 Wintech, 410
 Winkler and Koch, 265
 Wirtel, 300, 305, 309, 311, 312, 313, 315, 319, 321
 Wirth, 334
 Wischetravsky, 81, 155, 222, 468, 530, 531, 536
 Wischin, 381, 398
 Wismer, 226, 227
 Woelflin, 234, 252, 290, 344, 354, 355, 356, 369, 370, 371, 536, 545
 Wohlleben, 249
 Wolfson, 233
 Woo, 172
 Wood, 209
 Wood and Loomis, 166, 197
 Woodman, R. M., 38, 69, 162, 174, 175, 532
 Woog, 453, 455
 Worobjew, 233
 Worthington and Eddy (Petroleum Rectifying Co.), 353
 Wright, 39, 55, 75, 249, 254, 378
 Wyant, 346
 Wyatt, 227

Y

Young, 54, 115, 474, 498, 503
 Yuzhilm, 423

Z

Zaharia and Sucabu, 402
 Zalizetsky, 380, 526
 Zaliziecki and Brune, 527
 Zawidski, 121, 137
 Zelikow, 461
 Zhukow and Buschmakina, 11, 33, 36
 Zickermann, 193
 Zimmer, 463
 Zollman (Henrietta), 6
 Zsigmondy, 410
 Zwergel, 397, 402
 Zwilmeyer, 210

Subject Index

A

- Abietine, 312
- Abietinic acid, 185, 304, 318, 320, 410
- Acenaphthene, 325
- Acetaldehyde, 296
- Acetaldoxime, 128
- Acetals, 186
- Acetates, 27, 296
- Acetic acid, 41, 80, 124, 127, 128, 129, 176, 190, 191, 272, 274, 286, 305, 320, 325, 326, 383
 - anhydride, 305
- Acetone, 10, 30, 128, 178, 226, 233, 286, 299, 301, 383, 386, 411, 422, 431, 447, 535, 546
- Acetyl chlorides, 186, 195
 - oleic acid, 305
 - sulfonoleic acid, 305
- Acetylene, 544
 - tetrachloride, 411
- Acid amides, 182
 - binding agents, 181, 532
- Acidity, 177, 370, 441, 446, 459
 - of emulsions, 532
 - potential, 532
 - test, 532, 533
- Acids, 11, 27, 32, 46, 51, 80, 117, 159, 169, 171, 179, 180, 189, 325, 382, 404, 405, 407, 411, 413, 415, 441, 445, 449, 521, 526, 527, 533
- Acrylic acid, 181
 - nitrile, 181
- Activitv, 336
- Acy carbamic acid chloride, 192
- Aviation, 311, 318
- Adhesion, 125, 126, 136, 139, 151, 224, 455, 456, 493, 494
 - tension, 294
- Adsorbents, 275, 334, 335, 336, 337, 383, 385, 451, 456, 475
- Adorption, 73, 74, 98, 99, 125, 137, 138, 139, 163, 273, 275, 286, 289, 293, 296, 303, 334, 338, 383, 384, 385, 416, 433, 451, 457, 460
 - ability, 135, 385
 - agents, 335
 - equation, 385
 - films, 165, 454
 - Gibbs-Thomson principle, 72, 100, 101
 - heat of, 451
 - interfacial, 71, 72, 299
 - ionic, 51, 339, 515
 - isotherms, 100
 - layer, 137
 - molecular orientation in, 90-103
 - negative, 3
 - oppositional, 42
 - positive, 3, 122
 - preferential, 46, 85, 134, 150
 - selective, 13, 70, 271, 385, 451, 513, 545
- Agar-agar, 31, 33, 54, 174, 175, 178, 328
- Age-hardening, 400
- Aging of bitumen, 409
 - emulsions, 15, 17, 74, 88, 105, 353, 354, 531
 - interfaces, 90, 504, 531
 - oils, 459, 521
- Agitation, 202, 212, 219, 253, 263, 274, 277, 278, 283, 288, 298, 352, 379, 382
 - continuous and intermittent, 161, 162, 202
 - mode of mixing, 163, 164, 201, 202, 203, 289
 - paddling, 165
 - shaking, 161, 162, 163, 164, 166, 168, 254
 - stirring, 161, 163, 166, 199, 202, 206, 207, 208, 209, 210, 253, 265, 382, 526
- Air gas lift, 281
 - liquid interface, 19, 133, 136
- Albumen, 20, 29, 74, 456
- Albumin, 15, 20, 31, 72, 78, 103, 122, 124, 127, 182, 144, 148, 168, 170, 175, 177, 232, 271, 286, 376, 411, 423, 462
- Alcohols, 6, 19, 38, 49, 68, 80, 117, 118, 119, 121, 129, 143, 149, 169, 172, 174, 176, 179, 180, 181, 183, 185, 186, 188, 191, 193, 194, 195, 225, 232, 233, 274, 275, 286, 292, 299, 303, 304, 310, 312, 314, 319, 320, 324, 327, 330, 378, 382, 383, 407, 409, 410, 413, 434, 438, 439, 447, 455, 463, 494, 518, 521, 526, 527, 528, 535
- Aldehydes, 29, 169, 188, 298, 299, 301, 304, 319, 322, 324
- Alkol, 304, 312
- Algae slime, 178
- Algin, 417
- Alginates, 173, 174
- Aliphatic acid chlorides, 181
 - hydroaromatic hydroxyl compounds, 181
 - hydrocarbons, 380
- Alkali, 7, 10, 11, 12, 27, 32, 37, 38, 46, 48, 56, 69, 70, 78, 80, 86, 100, 107, 147, 159, 166, 170, 172, 174, 177, 178, 179, 188, 190, 191, 193, 196, 232, 275, 296, 297, 303, 305, 310, 314, 324, 325, 328, 338, 379, 381, 382, 401, 404, 405, 407, 409, 410, 411, 412, 413, 414, 415, 416, 420, 422, 427, 428, 429, 432, 434, 451, 463, 464, 528, 543
 - acetate, 329
 - bicarbonates, 417
 - borates, 171, 407
 - carbonates, 189, 407, 414, 417, 427, 432
 - caseinate, 421
 - content (free and total), 434
 - hydroxides, 195, 405, 406, 414, 415, 424
 - metals, 96, 187, 417, 549
 - naphthenates, 427
 - oleates, 404
 - phosphates, 190, 408
 - resinate, 175
 - silicates, 171, 405, 407, 415
 - thiocyanate, 305
 - thiosulfate, 305
- Alkaline earths, 26, 95, 191, 193, 286, 291, 296, 301, 305, 310, 312, 314, 405, 412, 421
 - hydroxides, 189, 428
 - oxides, 383
 - phenolate, 432
- Alkalinity, 370
- Alkaloidal bases, 179
- Alkyl amines, 192, 195, 299, 316
 - diluents, 182
 - isothioureaes, 185
 - mercaptans, 195
 - sulfates, 313
 - sulfuric acid, 194
- Alkylated aromatic hydrocarbons, 186
 - cellulose, 189
 - disulfides, 465
 - naphthalene sulfonic acids, 190
- Alkylation products, 320
- Alkylen oxide, 315
- Alkylol amine, 317, 318
 - aromatic sulfonamide, 319
- Allyl alcohol, 29, 169, 179
 - α -, β -, or γ -rays, 372
- α -ethyl acetate, 69
 - naphthyl ethers, 193
- Alum, 171, 176
- Alumina, 79, 370, 383, 432
- Aluminum, 65, 195, 295, 418, 433
 - chloride, 46, 47, 48, 50, 51, 186, 192, 196, 317, 407, 462
 - colloidal, 412
 - fluoride, 447
 - hydrate, 426

- Aluminum, hydroxide, 19, 97, 407, 411, 433
 oleate, 58, 96, 414, 419
 oxide, 171, 176, 294, 336, 427
 salts, 176, 186, 427
 stearate, 238, 419, 461
 sulfate, 10, 67, 171, 300, 323, 422, 427
 sulfonate, 189
- Amides, 188, 190, 191, 192, 193, 307, 312, 526
- Amines, 180, 181, 184, 190, 191, 192, 193, 195, 302, 306, 315, 316, 317, 318, 319, 321, 382, 426, 526
- Amino acids, 411
 alcohols, 193
 compounds, 169
- Ammoniates, 190
- Ammonium, 191
 amylamine, 326
 benzylamine, 326
 butylamine, 326
 chloride, 80, 165
 ethyl oleate, 327
 ferrous sulfate, 433
 fluosilicate, 421
 halogenide, 183
 hydroxide, 127, 173, 175, 184, 185, 188, 191, 303, 308, 309, 312, 314, 320, 323, 325, 407, 423, 433, 463, 464
 naphthenates, 414, 433
 oleate, 169, 297, 414
 oxystearate, 297
 ricinoleate, 304
 salts, 287, 313, 321, 409
 sulfate, 175, 310, 323, 403
 thiocyanate, 518
- Amonton's law, 453
- Amyl acetate, 12, 28, 74, 171
 amine, 321
 amino salt of cetylnaphthol sulfonic acid, 317
 alcohol, 28, 68, 117, 120, 128, 129, 131, 136, 148, 171, 172, 176, 179, 182, 190, 232, 299, 303, 462
 cyclohexylamines, 302
 naphthalene sulfonamide, 319
 phthalate, 318
- Amylene, 168, 384
- Anhydrides, 181, 186, 407, 411, 526, 527
- Anilide stearic acid, 178
- Aniline, 47, 54, 128, 129, 174, 179, 180, 190, 226, 302, 319, 322, 449
- Animal oils, 78, 177, 184, 195, 447, 449, 454, 533
- Anthracene oil, 309, 311, 314, 320, 427, 462
- Anthracite, 550
- Anthryl derivatives, 465
 valerate, 300
- Antifreeze agent, 463
- Antimony, 388
 chloride, 283
 sulfide, 383
- Antioxidants, 465
- Antonow's rule, 431, 449
- Arachic acid, 301
- Alkyl amines, 320
- Argon, 166
- Aromatic acids, 413
 arylated compounds, 169, 186
 hydrocarbons, 169, 190, 380, 384, 407, 426, 527, 552
 sulfonated compounds, 169
 sulfonic acids, 29, 415
 tar acid oil, 300
- Arsenic sulfide, 176
- Aryl dihydrogen phosphates, 179
 phenol, 318
 sulfonic acid, 313
- Asbestine, 426
- Asbestos, 428
- Ash, bone, 338, 339
 coal, 338
 content, 291, 333, 334
- Asphalt, 1, 12, 23, 30, 55, 76, 154, 168, 172, 173, 185, 190, 196, 197, 220, 228, 272, 273, 275, 396, 397, 398, 399, 411, 416, 426, 427, 428, 520, 522, 529, 536
 artificial, 398, 402, 404, 405, 411, 412, 427
 base oils, 397, 398, 405, 449
 chemical composition, 397, 398
- Asphalt, cut-back, 402
 dehydration, 403
 elasticity, 402
 flux oil, 423
 hard and soft, 168, 403, 427, 431, 459
 natural, 398, 402, 403, 404, 405, 413, 420, 427, 431
 production, 397, 402, 403, 404
 tests, 529
- Asphalt emulsions, 173, 186, 396-445, 411, 420, 524
 analysis of, 434-441
 emulsification, 399, 402, 403, 405-422
 emulsifiers, 405, 406, 407, 408, 409, 410, 411, 412, 413, 414, 415, 416, 417, 418, 420, 421, 424
 equipment used, 406, 419, 420, 421
 methods of use, 396, 397
 properties, 400, 401, 402
 stabilization, 421-427
 stabilizers, 405, 406, 416, 417, 421, 422, 423
 tests, 440, 441, 524, 525
 asphalt-bitumen content, 434
 alkali (free and total), 434
 coating, 440
 demulsibility, 437, 438
 distillation, 436
 ductility, 435, 436
 emulsifying agent, 434
 freezing, 440
 penetration, 435
 sedimentation, 436, 437, 440
 sieve, 440
 softening point, 435
 stability, 438, 439, 440
 viscosity, 436
 water content, 434
 weathering, 401
- Asphaltenes, 55, 273, 398, 402, 405, 459
- Asphaltic acids, 413
 base, 286, 334, 382, 404
 base oils, 286, 332, 414
 crude oil, 369
 resins, 398
- Association coefficients, 226
- Atomization, 163, 197, 203, 254, 292, 340, 354, 378
 cathodic, 198
- Azelaic acid, 306
- Azerole green dye, 298

B

- Babcock test, 492
- Balloelectric effect, 135
- Bancroft's rule, 30, 96, 101
- Barium, 328
 chloride, 46, 47, 48, 50, 176, 408, 430, 434
 nitrate, 67
 oleate, 298
 salts, 232, 528
 sulfate, 326, 338
 sulfonate, 189
- Bartell's method, 446
- Bauxite, 336, 384
- Bentonite, 68, 173, 294, 383, 408, 410, 411, 422, 424, 426, 429, 436
- Benzaldehyde, 304
- Benzene, 6, 10, 11, 12, 19, 21, 22, 23, 28, 29, 30, 36, 47, 54, 60, 63, 64, 66, 67, 68, 69, 74, 77, 80, 81, 84, 89, 90, 98, 100, 127, 128, 161, 162, 163, 166, 169, 172, 175, 176, 179, 180, 182, 183, 190, 192, 195, 197, 226, 233, 274, 275, 286, 287, 292, 300, 308, 309, 311, 312, 314, 319, 324, 327, 338, 382, 384, 386, 408, 409, 415, 422, 431, 434, 447, 451, 459, 462, 464, 501, 528, 531, 532, 535, 538, 541, 542, 543, 544, 545, 546, 549
 sulfonate, 183
 sulfonic acid, 308
 sulfo-stearic acid, 237
- Benzine, 19, 24, 274, 275, 304, 384, 542
- Benzoic acid, 184, 185
- Benzonitrile, 47, 169, 526
- Benzyl, 30
 alcohol, 29, 120, 128, 129, 169, 196
 amine, 315, 316, 321
 aminopropane-2, 3-diols, 316

- Benzyl, amino-2-propanol, 316
 amylbutyl naphthalene, 169
 butyltetralin, 169
 cyclohexyl naphthalene, 169
 Benzylidene aniline (Schiff's bases), 181
 Berlin blue dye, 411
 β -halide ethane sulfonic acid, 182
 naphthol, 300, 314
 naphthol ester, 304
 naphthol sulfonic acid, 29
 sulfio ethyl esters, 313
 Beryllium fluoride, 447
 Bicarbonates, 325, 330
 Bile, 175
 acids, 421
 anions, 168
 Bimolecular leaflet, 99, 100
 Binding agents, 177, 432, 521
 Bisamylamino-2-propanol, 316
 Bisdiamyl-2-propanol, 316
 Bisulfite, 313
 Bitumen, 170, 171, 173, 174, 176, 177, 178, 179,
 188, 189, 202, 322, 338, 384, 397, 398, 399,
 400, 403, 405, 406, 409, 411, 416, 421, 422
 emulsions, 171, 173, 399
 breakability of, 439
 emulsification, 405-422
 emulsifying agents, 409, 410, 411, 412, 413, 414,
 415, 416, 417, 418, 419
 equipment, 419, 420, 421
 for road construction, 426-430
 stability, 429-434
 tests, 433, 434
 Black contact (sulfonic acids), 310
 spots, 144, 147
 Bleaching agents, 465
 powder, 295, 330
 Blown castor oil, 304, 309, 320, 321
 oils, 320, 321
 products, 309
 Borates, 183, 403, 411, 414
 Borax, 174, 322
 Boric acid, 191, 194, 273, 317, 322
 anhydride, 322
 Boron chloride, 322
 fluoride, 308, 322, 447
 Borosilicate, 171
 Bottom settlements, 220, 221, 234, 239, 241, 276, 297,
 311, 322, 371, 374
 Boundary heterogeneity, 122, 123, 124, 125, 126,
 127, 138, 149
 tension, 503, 531
 Brass, 19, 520
 Break-down voltage, 519
 Breaking index, 439
 Brine, 249, 275, 282, 298, 326, 329, 333, 532, 536
 Bromide, 328
 Bromine, 28, 321
 Bromobenzene, 226
 Bromoform, 43
 Bronze, 452
 Brownian movement, 2, 3, 43, 48, 51, 57, 63, 106,
 137, 160, 227, 480, 492
 Bubble-pressure method, 495, 496
 Butane, 413, 428
 Butanone, 431
 Butyl alcohol, 169, 172, 182, 184, 185, 190, 193, 303,
 307, 308, 322, 326
 aldehyde, 304
 benzene, 186
 cyclohexylamines, 302
 naphthalene sulfonic acid, 106
 phthalate, 303, 318
 tetrahydro-naphthalene carboxy acid, 302
 Butyrate, 27
 Butyric acid, 91, 117, 118, 120, 128, 129, 312, 325,
 454

C
 Cadmium, 455
 Caffeine, 449
 Calcium, 78, 287, 328, 379, 383, 534
 acetate, 439
 arsenate, 29
 Calcium, carbide, 544
 carbonate, 29, 181, 249, 295, 326, 336, 414, 417
 caseinate, 170
 chloride, 63, 71, 144, 249, 286, 291, 293, 326, 329,
 333, 383, 412, 413, 421, 422, 423, 427, 430,
 434, 437, 438, 440, 464, 533, 544, 546
 cresolate, 297
 fluoride, 326
 hydroxide, 300, 408, 412, 425, 427
 hypochlorite, 295
 iodide, 28
 naphthenates, 310, 425, 427
 oleate, 63, 62, 63, 64, 208, 378
 oxalate, 534
 oxide, 425, 438, 462, 463
 phosphate, 412
 resinate, 421, 422
 salts, 173, 189, 232, 325, 403, 405, 415
 sulfate, 176, 249, 310, 430
 sulfonates, 310
 Calomel cell, 534
 Camphor, 447
 Canal rays, 372
 Capillarity, 493, 498
 Capillary-active molecules, 494
 substances, 116, 117, 118, 121, 122, 124, 127,
 128, 148, 149, 150, 327, 494, 506
 activity, 120, 494
 phenomenon, 12
 pressure, 101, 143
 rise method, 494, 495
 Capric acid, 455
 Caproic acid, 117, 128, 129
 Caprylic acid, 29, 125, 128, 129, 169
 Carbocyclic compounds, 179
 Carbohydrates, 168, 179, 193, 299, 397, 398, 423
 Carboic acid, 304, 432, 462
 Carbon, 25, 80, 125, 176, 334, 397, 398, 459, 534
 activated, 335
 black, 10, 66, 68, 81, 176, 545
 colloidal, 196, 397, 398
 dioxide, 148, 210, 299, 321, 325, 327, 349, 369, 397,
 458, 528, 549
 disulfide, 28, 182, 185, 226, 286, 431, 545
 iodide, 81
 monoxide, 397
 residue test, 529, 554
 tetrachloride, 12, 28, 54, 61, 68, 69, 174, 185, 286,
 296, 302, 317, 327, 353, 411, 431, 545
 Carbonates, 183, 249, 288, 411, 434
 Carbonic acid, 287
 Carbonization, 187
 Carboxylic acid, 169, 181, 182, 185, 186, 188, 191,
 192, 193, 195, 301, 302, 303, 304, 307, 308, 312,
 318, 319, 320, 411, 462, 525
 amide, 183
 anhydrides, 182
 butyl cyclohexanol, 169
 halides, 182
 fatty, 190
 isopropyltetrahydronaphthalene, 169
 propyl cyclohexanol, 169
 Casein, 10, 11, 28, 29, 31, 75, 78, 97, 149, 168, 170,
 174, 175, 177, 182, 232, 326, 404, 406, 407,
 411, 412, 413, 416, 417, 421, 423, 426, 427,
 438
 Cassel's theory, 101
 Castor oil, 16, 38, 90, 112, 165, 173, 180, 187, 193,
 233, 288, 298, 299, 300, 303, 304, 305, 306, 308,
 309, 313, 318, 321, 322, 426, 447, 451, 454
 Catalysts, 189, 397, 459, 462
 alkali, 184
 aluminum chloride, 322
 borax, 322
 boric acid, 322
 boron chloride, 322
 boron fluoride, 322
 calcium naphthenate, 425
 copper hydroxide, 465
 iron chloride, 322
 molten metals, 385
 molybdenum oxide+hydroxides (Co, Cr, Al),
 465
 nickel, 186
 nickel hydroxide, 465

- Catalysts**, Petrow's and Twitchell's, 180
 potassium soap, 187
 sodium carbonate, 183
 tin alloy, 385, 386
 zinc chloride, 322
Cataphoresis, 2, 42, 44, 45, 47, 85, 342
Cataphoretic mobility, 44, 47, 48, 135, 339
 separation, 341, 350
 streams, 515
 velocity, 51, 52
Cathode rays, 372
Cedar oil, 112, 480
Celite, 337
Cellulose, 173, 177, 232, 292, 397, 398, 406, 451, 515
 films, 74
 method, 186
 nitrate, 74
 sulfite, 172, 187, 190
Cements, 396, 408
Centrifugal subsidence, 375, 378, 386
Centrifugeable solids (in crude oil), 533, 535
Centrifuges, 374, 378
 bottom-discharge, 377
 continuous and non-continuous, 374, 376
 electrically-driven, 377
 steam-driven, 377
 super, 270, 374, 377, 378, 379
 ultra, 59, 373, 374, 486
Cerealian, 409
Ceresin emulsions, 323
Cesium, 328
 oleate, 96
 palmitate, 57, 97
Cetene, 196
Cetyl alcohol, 102, 186, 194, 196
 bromide, 319
 naphthol sulfonic acid, 317
 phenol, 218
 phenol sulfonic acid, 317
 pyridine bromide, 319
 sulfate, 168
 sulfonic acid, 312
Chains, 339, 340, 512, 526
 detective, 340
 length, 494
Chalk, 79
Charcoal, 459
 active, 433
 blood, 338, 383
 bone black, 383
 wood, 338
Charitschkoff's copper reaction, 78
Chinawood oil, 322
Chloranhydrides, 527
Chlorhydrines, 308, 315, 316
Chlorides, 186, 249, 328, 533, 534
Chlorination, 426, 455
 products, 320
Chlorine, 28, 232, 302, 308, 311, 321, 411, 433
Chlorobenzene, 169, 228
Chloroform, 28, 29, 47, 54, 60, 174, 175, 185, 226, 431
Chlorofumaric acid, 192
Chlorosulfonic acid, 189, 191, 192, 194, 195, 312, 313, 317, 320
Chlorotolyl ether, 193
Cholesterin, 233
Cholesterol, 16, 29, 64, 65, 102, 168
 acetate, 168
 stearate, 168
Chromium, 295
 green, 411
 yellow, 411
Chrysene, 2
Citric acid, 303, 304, 417, 422, 423
Citron oil, 381
Clausius-Mosotti equation, 47
Clay, 29, 80, 154, 173, 176, 202, 210, 264, 286, 294, 337, 338, 370, 401, 404, 408, 409, 410, 411, 414, 417, 418, 422, 423, 424, 427, 428, 435, 475
 blue, 398, 429
 china, 383
 colloidal, 398, 403, 415, 416
Cloud- and pour-point tests, 557, 558
Coagulation, 8, 48, 50, 51, 52, 175, 271, 300, 339, 340, 341, 354, 369, 370, 404, 421, 422, 430, 432, 433, 438, 440, 480
 agent, 400, 433
 mechanical, 162, 253, 382
 of emulsions, 47
 of foams, 131
Coal, 383, 412, 413, 415, 417, 423, 426, 462
 oil, 171
 tars, 12, 171, 177, 179, 187, 190, 196, 197, 250, 306, 309, 322, 348, 377, 423, 426, 428, 429, 434, 447, 462, 463, 464, 545
 tar dyes, 78
Coating test, 440
Cobalt, 296
 acetate, 296
 formate, 296
 oxalate, 296
 oxide, 296
 tartrate, 296
Cocunut oil, 194, 302
Cod liver oil, 90
Coefficient of static friction, 450, 454, 455
Cohn's rule, 40, 41
Cohesion, 14, 73, 126, 136, 138, 139, 142, 143, 150, 224, 225, 493, 494
 pressure, 452
Coke, 323, 326, 330, 383, 397, 423, 458, 459
Collochon, 27
Colloidal metals, 43, 54
Colloid-electrolytes, 25
Colloid mills, 162, 171, 199, 200, 201, 406, 407, 410, 414, 415, 419, 421, 423
 kinds:
 Charlott, 200
 Hurrell, 200, 406
 Premier, 200
 Rex, 201
 types:
 beater, 199
 centrifugal smooth-surface, 199, 200
 rough-surface, 200
 smooth-surface, 199
Colophonum, 411
Colophony, 413, 415, 447
Compounded oils, 446
Compressibility definition, 456
 of liquids, 456
 test, 456
Condensation, 163, 182, 183, 186, 188, 189, 191, 192, 193, 194, 299, 301, 303, 313, 315, 318, 319, 320, 382, 384, 397, 421, 434, 458, 462, 470, 549
 products, 181, 193, 301, 311, 312, 313, 314, 316, 320
Conductivity, 9, 26, 253, 295, 348, 356, 357
Congo red dye, 72, 180
Conoco germ-process oil, 446
Conradson's test, 460, 523, 525
Contact angle, 81, 82, 104, 451, 452, 453, 505
Copper, 81, 269, 295, 433, 471, 455, 458, 517, 518
 bromide, 424
 chloride, 518
 chromate, 421
 fluoride, 424
 hydroxide, 424, 433, 465
 nitrates, 424
 oxide, 253
 pyrites, 124, 138
 salts, 176, 528
 sulfate, 10, 56, 79, 326, 424, 518, 546
 sulfide, 19
 thioevanate, 424
Cork, 294
Corn oil, 303, 309, 320, 322
Corrosion, 197, 287, 291, 310, 329, 331, 332, 333, 411, 424, 457, 462, 532
Cotton, 370, 428, 458
Cottonseed oil, 15, 54, 73, 165, 187, 303, 309, 322, 414, 422, 447
Coumarone, 413
Cracking, 251, 328, 333, 383, 397, 401, 402, 404, 462, 465, 554
Creosote oils, 80, 180, 184, 185, 196, 322, 325, 462, 540

- Cresosap (automatic emulsifier), 54, 475
 Cresol, 30, 54, 69, 120, 128, 129, 148, 172, 180,
 184, 185, 196, 274, 290, 309, 317, 322, 326,
 412, 428, 475
 disulfonic acid, 326
 Cresylic acid, 69, 162, 173, 178
 Critical geometrical point, 61
 Crotonic acid, 454
 aldehyde, 304
 Crude oil emulsions, 2, 30, 222, 228, 244, 272, 274,
 302, 309, 310, 322, 324, 325, 342, 344, 347,
 348, 353, 374, 375, 378, 386, 404
 Crude oils, 30, 55, 154, 190, 211, 212, 265, 266
 297, 329, 330, 334, 335, 413, 434, 457, 520,
 529, 532, 534, 535, 536, 543, 545
 American, 553
 Argentine, 397
 Arkansas, 332
 Baku, 81, 219, 291, 325, 382, 384
 Bibi-Eibat, 77, 302, 310, 381
 Boryslaw (Kalropony), 221
 Buena Vista, 477
 California, 228, 229, 230, 336, 337, 352, 355, 357,
 365, 384, 397, 548
 Casmalia, 229, 479
 Caspian Sea, 302
 Colorado, 211, 219
 Columbia, 397
 Coyote Hills, 478
 Elkhills, 476, 481, 482
 Galician (Czeizowica), 221, 381, 402
 Grozny, 323, 381, 528
 Hungarian, 381
 Kansas, 329, 376, 379
 Kurakawe, 397
 Louisiana, 397
 Mexican, 234, 377, 397, 403
 Michigan, 330
 Mid-Continent, 548
 Nizhny-Novgorod, 382
 Oklahoma, 157, 211, 219, 272, 376, 379, 529, 548,
 551
 Pennsylvanian, 402
 Roumanian, 380, 402, 526, 553
 Russian, 553
 San Joaquin Valley, 474, 524
 Sakhalin, 397
 Santa Maria, 229, 230, 231, 334
 Ssurachan, 381
 Texas, 157, 211, 219, 260, 274, 330, 376, 397, 463,
 551
 Trinidad, 397
 Tschaleken Island, 302, 528
 Tzaritzin (Kala), 291, 292, 325
 Utah, 219
 Wyoming, 211, 219, 551
 Crvstal violet dye, 228
 Curvature method, 496
 Curves, derivative, 59, 483
 differential, 59, 484, 485, 486, 487, 488, 489, 490,
 491
 flow, 440
 foam formation-concentration, 117
 integral, 59, 484, 485, 486, 487, 488, 489, 490, 491
 Maxwell distribution, 429
 number distribution, 58, 59, 88, 89, 96, 97, 105,
 480, 483, 486
 pressure-volume, 226
 surface tension-concentration, 122
 viscosity, 552
 viscosity-temperature, 449
 weight-optical distribution, 59, 60, 486, 491, 492
 Cut oil, 220, 221, 260, 263, 285, 289, 357, 361, 364,
 536, 537
 Cutting oils, 8, 9, 445, 463
 Cyclic alcohols, 416
 hydrocarbons, 180, 462, 526, 552
 sulfonic acids, 320
 Cyclo-alkyl sulfonic acid, 185
 alkyl amines, 320
 hexane, 431, 525
 hexanol, 30, 178, 179, 181, 190, 298, 312, 313
 hexanone, 179, 190
 hexene, 312
 hexyl amino salts, 314, 315, 317
 Cyclo-hexyl amino-2, 3-propanediol, 315
 hexyl benzene, 186
 olefins, 823
 pentamethylene, 525
 Cylinder oil, 45, 46, 54, 397, 463, 553
 distillates, 67
 Cymene, 308
- ## D
- Deaminization, 171, 174
 Debye's theory, 520
 Decanaphthenic acid, 527
 Decarboxylation, 308
 Decolorizing agents, 383, 384, 385, 463
 Degree of demulsibility, 524
 dispersion, 16, 17, 31, 38, 48, 98, 104, 105, 131,
 134, 137, 140, 150, 153, 163, 181, 201, 223, 341,
 375, 401, 404, 431, 438
 emulsification, 165
 hydration, 31, 32
 stability, 105, 130, 222, 530
 Dehydrating agents, 193, 195, 296, 314, 397, 545
 Dehydration of emulsions, methods of, centrif-
 ugal, 372-380
 chemical, 270-326
 and heat treatment, 282
 dilution, 328
 electric, 267, 300, 338-373, 523
 alternating current, 339, 341, 343, 345, 346,
 347, 351, 355, 358, 359, 360
 direct current, 341, 350, 371
 electro-osmotic, 349
 equipment and processes, 344-373
 mechanism, 338, 339, 340, 341
 pulsating current, 350
 tank method, 368
 filtration, 334-339
 and electric treatment, 370
 freezing, 327, 328
 heat, 222-253
 and centrifuging, 264, 268, 269, 270, 371
 and filtering, 268
 and mechanical treatment, 253-264
 and pressure, 264-269
 and electric treatment, 369
 equipment, 234-253
 indirect heat treatment, 249-253
 with distillation, 246-250
 magnetic, 372
 mechanical, 258-264
 excelsior systems, 258, 259, 260
 water-knockout systems, 258, 260, 261, 262,
 263
 rays, 372
 ultrafiltration, 337, 338
 Dehydration of foaming oils and tars, 147, 149
 Dehydrators, 223, 356
 Cage, 348, 358
 CF, 343, 351, 358
 Cottrell, 342, 343, 344, 345
 C. R., 343, 360
 D. T. C. R. P., 361, 362
 Flow-line, 362, 363, 364, 365, 367
 H. C. F. P., 359
 H. F., 343, 345, 346, 352
 Metan, 237, 266
 Miniature, 530
 National, 342, 343, 344
 Petresco, 364, 365, 366
 Dehydrogenation, 308, 397
 Dehydroxylation, 300, 301, 313
 Demulsibility of oil, 460, 461, 522
 Demulsification, 219-396, 522
 limits, 523
 tests, 460, 524, 525
 time, 13
 value, 446, 460
 Demulsifiers, 270-326
 acid and alkali sludge, 323
 acids, bases and salts, 291, 292, 293
 alcohols, 299
 blown oils, 320, 321, 322
 colloids, 297

- Demulsifiers, commercial, 286, 208
 condensation products of organic compounds, 301
 cracked residues, 325
 distillation products, 322
 gases, 295-297
 hydroxy-derivatives of organic compounds, 300, 301
 organic acids, salts, 301-309
 paraffin, wax, etc., 322, 323, 324, 325
 soaps, 297, 298
 solids, 293, 294, 295
 sulfonated compounds, 308-321
 tests, 529, 530
- Densitv, 143, 166, 270, 354, 356, 371, 373, 500, 541, 551, 552
- De-oiling of waxes, 198
- Deparaffination, 378
- Depolymerization, 191
- Derivative curve construction (S. Berkman), 483, 486
- Desalting, 295, 329-335, 365, 386
 electric, 333, 334
 heat, 330, 331, 332, 333
 influence of temperature and pressure, 334
 plants, Petreco electromatic, 332, 333
- Desulfurization, 383
- Dextrin, 20, 31, 33, 75, 133, 149, 168, 170, 179, 232, 413
- Dialkyl-naphthalene disulfonic acid, 319
 polysulfonate, 314
- Dialysis, 27
- Diamines, acylated, 180
- Diamylaminopropane-2, 3-diol, 316
- Dicyclopentadiene, 381
- Diaryl ethane, 169
 hydrogen phosphate, 179
- Diatomaceous earth, 294
 silica, 385
- Dicarboxy acid, 306
- Dichlor ethylene, 296
 hydrine, 315, 316
- Dielectric barrier, 349, 350, 354
 characteristics, 351
 constants, 41, 44, 45, 46, 47, 49, 153, 271, 340, 341, 342, 434, 509, 513, 515, 516, 519, 520, 521
 of air, 520
 hydrocarbon-cellulose, 521
 petroleum products, 520, 521
 transformer and switch oils, 520
 phase, 197
 properties, 357
 strength, 356, 519, 520
- Diethanolamine, 307
- Diethyl cyclohexylamine, 315
 ether, 538
 sulfide, 312
- Diethylene glycol, 305, 308
- Diffusion, 27, 51, 89, 99, 103, 134, 160, 172, 280, 325, 327
- Diglyceride, 305
- Diglycerin, 319
- Diglycerol, 185
- Dihexyl ester, 313
- Dihydro-dioxylene, 174
 oxynaphthalene, 314
- Diisopropyl-naphthalene sulfonic acid, 314
- Diluting agents, 189
- Dilution, 96, 144, 178, 274, 480, 545
- Dimethyl aniline, 43, 68, 69, 181
 aniline-benzene, 12
 heptane, 12
 sulfate, 193
- Dimeric interface, 80, 82, 500, 501
- Diolefins, 384, 404
- Dioxan, 183
- Dioxyalyl-triricinolein, 305, 313
- Dioxyhendecenoic acid, 306
- Dioxytenuic acid, 187
 amide, 303
- Dipentenes, 384
- Diphenyl, 190, 415
 amine, 319
- Dipole, 286, 493, 514
 directed, 49
 effect, 49
 molecules, 49
 moments, 286
- Diricinolein, 306
- Dispersing agents, 8, 180, 183, 185, 233, 409, 426
- Distribution coefficient of emulsifier, 162
 soap, 61, 70
 equilibrium, 70
- Dodecylsulfuric acid ester, 185
- Dodecylene, 308
- Dolomite, 411
- Drop number, 498, 503
 pipette, 502
 weight method, 498, 499, 500
- Dual phenomenon, 404
- Ductility, 435, 436, 440
- Dupré's equation, 126
- Dyestuffs, 180, 228, 494

E

- Earths, 383, 422, 429, 465
 Florida, 461
- Ebullition, 224, 225, 226, 227, 228, 269
- Egg-yolk, 168, 175
- Elasticity, 130, 133, 149, 150, 400, 402
- Electric charge, 13, 14, 26, 31, 40-54, 65, 270, 271, 286, 296, 416, 419, 430, 509
 conductivity, 515, 519, 521, 531
 dispersion, 197
 double-layer, 40, 43, 44, 48, 49, 50, 51, 105, 106, 107, 136, 509, 513, 514, 515
 Gouy's diffuse, 42, 43, 509, 510, 514, 515
 Helmholtz, 42, 44, 52, 53, 514, 515
 Stern's, 514
 endosmosis, 41, 45, 47
 pressure, 14
 space charges, 348
- Electrodes, 341, 342, 343, 344, 345, 346, 347, 348, 349, 350, 352, 353, 357, 358, 359, 369
 antimony, 512
 C. R. type, 352, 361, 362
 glass, 511, 513
 Beckman's, 513, 533
 Coleman's, 512
 Haber and Klemensiewicz, 136, 510
 Hellige, 512
 HCF, 359, 362
 HF, 359
 hydrogen, 533
 normal, 511
 platinum black, 533
 quinhydrone, 512, 533
- Electrolysis, 342
- Electrometric titration, 534
- Electronic effect, 44
- Electro-osmosis, 349, 515
- Electrophoresis, 515
- Elektron process, 462
- Emulsification, 4, 5, 6, 7, 9, 10, 11, 12, 15, 19, 20, 21, 23, 29, 32, 33, 36, 38, 42, 48, 53, 54, 56, 57, 58, 60, 61, 63, 66, 67, 68, 69, 70, 71, 80, 81, 84, 85, 98, 99, 100, 103, 104, 107, 148, 153-219, 299, 379, 386, 405
 equipment, 199-211
 high-pressure, 203, 204
 with application of centrifugal force, 204, 205, 206
 mechanism, 153-161, 208
 methods of, 161-168
 processes, 167, 197-199
 values, 460
- Emulsifying agents, 5, 10, 15, 16, 20, 23, 24, 25, 26, 27, 28, 29, 30, 33, 36, 38, 42, 48, 53, 54, 56, 57, 58, 60, 61, 63, 66, 67, 68, 69, 70, 71, 72, 75, 78, 79, 80, 83, 84, 85, 88, 89, 92, 93, 95, 96, 97, 98, 101, 103, 104, 105, 107, 130, 153, 160, 165, 167-198, 401, 525
 colloids, 173-177
 electrolytes, 171-173
 gums, 178
 oils and prepared emulsions, 196-198
 organic compounds, 169, 178-189
 resin soaps, 176-178

Emulsifying agents, sulfonated products, 189-197
 sulfonic acids and sulfonated oils, 187-189
 Emulsions, alkaline, 275
 artificial, 189, 221, 475
 color, 221, 273
 concentrated, 112
 dual, 68, 69, 107, 173, 174, 532
 loose and tight, 220, 274, 474
 quasi, 78, 79, 156
 semi-solid, 220
 stiff, 159, 178, 178, 297, 302
 transparent, 475
 type test, 531, 532
 Emulsor (de Laval), 208
 Energy, 135
 boundary, 138, 151, 493
 free, 139
 kinetic, 99, 128
 mechanical, 166
 potential, 3, 99
 surface, 98, 99, 125, 126
 Eosin, 172
 Equilibrium, dynamic, 58, 129, 134, 140, 150, 151,
 153, 366
 of emulsion, 70, 93, 160
 static (durable), 58, 105, 129, 140, 150
 Esterification, 181, 182, 184, 185, 186, 190, 192,
 194, 299, 301, 303, 305, 306, 312, 318, 319, 320,
 322, 326
 Esters, 29, 117, 169, 172, 180, 183, 185, 186, 188,
 189, 190, 191, 192, 194, 195, 287, 299, 300,
 301, 303, 304, 306, 308, 311, 312, 313, 314,
 318, 319, 321, 327, 407, 410, 455, 521
 Estolides, 321
 Ethane, 369, 413, 428
 Ethanolamine, 321, 463
 Ethereal oils, 381, 382
 Ethers, 6, 30, 132, 171, 181, 182, 184, 185, 186, 187,
 188, 193, 194, 226, 274, 275, 286, 302, 305,
 308, 312, 315, 431, 456, 527, 528, 543
 Ethyl alcohol, 29, 30, 120, 128, 129, 169, 176, 177,
 182, 194, 226, 233, 200, 309, 320, 326, 329
 415, 426, 431, 533, 546
 acetate, 25, 171, 174, 191, 431
 amine, 123
 dichlorostearate, 455
 ester, 194
 ether, 226, 403
 naphthalene, 326
 propionate, 128
 Ethylene glycol, 187, 193, 305, 306, 308, 463
 ditolyl ether, 193
 oxide, 301, 315, 316
 Eucalyptus oil, 131
 Evaporation, 142, 144, 147, 150, 223, 224, 225, 227,
 229, 232, 386, 450, 486, 544, 554
 Evaporators (multiple-effect), 246, 266, 269

F

Fats, 11, 29, 147, 149, 169, 174, 175, 178, 179, 180,
 183, 184, 188, 189, 190, 193, 196, 232, 238,
 268, 292, 301, 309, 310, 410, 411, 412, 413,
 420, 427, 429, 445, 447, 523, 525, 540
 splitting agents, 189
 Fatty acid halides, 183
 acids, 4, 5, 8, 11, 25, 26, 27, 37, 38, 56, 66, 70,
 86, 87, 94, 107, 118, 119, 129, 137, 165, 170,
 171, 175, 176, 177, 178, 179, 180, 181, 183,
 184, 185, 186, 187, 189, 191, 192, 193, 194,
 195, 227, 232, 233, 273, 287, 288, 297, 299,
 300, 301, 302, 308, 304, 306, 309, 310, 312,
 314, 317, 319, 320, 380, 383, 397, 405, 406,
 407, 408, 409, 412, 414, 416, 420, 427, 428,
 445, 450, 454, 455, 459, 461, 464, 494, 525,
 526, 533, 535
 alcohols, 194
 aldo-fatty acids, 324
 amides of fatty acids, 303, 318
 amino-fatty acid, 302
 glycerin, 302
 hydroxylated fatty acid, 304
 keto fatty acid, 305, 306
 poly-keto fatty acid, 300
 oils, 170, 174, 188, 322, 408, 428, 447, 449, 451,
 461

Feldspar, 124, 148
 Fermentation process, 148
 products, 299
 Ferments, 197
 Films, 73, 77, 100, 142, 327, 342, 396, 399
 coherent, 74, 80, 84, 90, 270
 curvature, 93, 95, 96, 97, 101, 104, 106
 elastic, 78
 in emulsions, 74, 80, 84, 90, 91, 92, 93, 94, 95
 in foams, 115, 122, 136, 137, 140
 protective, 78, 270, 272, 285, 286, 292, 405, 406
 thickness of (in emulsions), 85, 86, 87, 88, 89,
 91, 106, 107, 124, 448, 453, 454, 455, 531
 thickness of (in foams), 115, 138, 139, 140, 141,
 143, 144, 145, 146, 150
 Fire extinguishers, 148
 Fish oil, 40, 175, 187, 321, 322, 427, 447, 462, 521
 Flash- and cloud-point tests of oil, 555, 556
 Flaxseed oil, 297, 309
 Flintstone, 370
 Flocculating agents, 52, 81, 97, 286, 294, 400, 401,
 431
 Flocculation, 52, 53, 328, 431
 Floridin, 338, 384, 446
 Floss silk, 370
 Flotation process, 12, 125, 134, 148, 150
 Fluorene, 2
 Fluorescence, 1, 2
 Fluorine silicate, 421
 Foam, 112-153, 247, 354
 formation, 112, 113, 114, 115, 116, 117, 118, 119,
 120, 121, 122, 124, 130, 131, 133, 134, 147, 148,
 149, 150, 180, 207, 228, 229, 230, 231, 232, 233,
 269, 369
 prevention, 147, 148, 149, 231, 232, 233, 247, 266,
 421, 539, 541, 542
 stability, 128, 129, 130, 131, 132, 133, 134
 Foaming ability, 120, 121, 122, 123, 125, 129, 140,
 149, 227, 233, 528
 agents, 120, 121, 124, 125, 129, 130, 132, 134,
 139, 148, 149, 151, 191, 195, 322, 327
 Forces, adhesion, 4, 92, 126, 225, 334
 adsorption, 451
 affinity, 334, 335, 455
 capillary, 51, 106, 112, 130, 135, 136, 140, 150,
 326, 335, 338
 centrifugal, 145, 147, 373, 374, 375, 376, 377
 centripetal, 147
 chemical, 41, 334
 cohesion, 4, 14, 92, 105, 126, 133
 electrical, 106, 130, 136, 339
 electromagnetic, 140
 electrostatic, 43, 135, 140, 150, 341, 342
 gravitational, 6, 56, 100, 104, 140, 373, 375
 interfacial, 100
 mechanical, 61, 135, 156
 physical, 334
 physico-chemical, 451, 455
 shearing, 84, 201
 van der Waals, 101
 Formaldehyde, 183, 188, 296, 301, 312, 421
 Formates, 296
 Formic acid, 128, 129, 325
 Formalin, 296, 381
 Formolin, 384
 Froth, 125, 134, 150, 163
 formation, 100, 233, 404, 540
 disintegrating tubes, 248
 Fructose, 175, 179
 Fuel, 210
 oil, 171, 324, 382, 422, 447, 535
 Fuller's earth, 171, 173, 275, 336, 337, 338, 383,
 384, 422, 446, 459, 463, 529
 Fumaric acid, 303, 304
 Furfural, 298, 304, 415, 422, 427, 428
 Furfuraldehyde, 173
 Furfural, 413
 Furfuryl, 192

G

Galena, 124, 125, 128
 Gallio acid, 174
 Gamboze, 18, 52, 53, 174, 177
 γ -4-butylphenyl- γ -oxybutyric acid, 186
 γ -cyclohexylphenyl- γ -oxybutyric acid, 186
 hydroxyquinoline method, 534

- Garnet, 294
 Gas, 134
 anchors, 158, 263
 emulsion mixture, 354
 generator, 369
 inert, 321, 369
 oil, 67, 263, 323, 447
 tar, 314, 323, 377
 tar emulsions, 156, 256, 267, 274, 377, 420
 Gases, 137, 155, 290, 349, 350, 353, 354, 364, 368, 369, 370, 371, 404, 427, 458, 462, 473, 475, 524
 Gasoline, 55, 56, 76, 77, 155, 166, 286, 287, 310, 326, 375, 379, 402, 404, 431, 447, 520, 539, 545, 546, 554
 carbon disulfide, 538
 diethyl ether, 538
 emulsions, 21, 55
 Gauger's test, 238
 Gauges, bottom-hole pressure, 471
 open type, 473
 vapor-tight, 473
 Gel, 1, 31, 176, 220, 221, 273, 335, 411
 formation, 2, 20, 177
 Gelatin, 11, 20, 21, 22, 28, 29, 31, 32, 33, 36, 38, 52, 54, 69, 90, 132, 149, 162, 167, 168, 170, 171, 174, 175, 178, 187, 195, 198, 232, 297, 326, 378, 406, 411, 456, 531
 Gelatinization, 2, 273, 327, 335
 Gelatins, 168
 Gibbs' adsorption layer, 124, 127, 129, 137
 equation, 61, 71, 72, 122
 theory, 5, 76, 77, 122, 123
 Glass, 19, 41, 76, 81, 137, 205, 293, 294, 337
 wool, 137, 370
 Glauber's salt, 174, 372
 Gliadin, 168
 Glues, 29, 78, 103, 147, 174, 177, 178, 182, 189, 195, 198, 233, 297, 376, 407, 410, 411
 animal, 232
 bone, 232, 410
 Glutaric acid, 303
 Gluten flour, 413
 Glycerides, 180, 188, 300, 312, 319, 427, 447, 449, 454
 Glycerin, 7, 13, 15, 69, 117, 175, 177, 179, 182, 183, 187, 198, 292, 297, 299, 305, 306, 309, 310, 315, 318, 319, 321, 322, 329, 330, 378, 463
 chlorhydrine, 303
 dichlorhydrine, 308
 monoxylenyl ether, 194
 ricinoleic acid ester, 191
 sulfo-acid triamylamine, 318
 Glycerol, 29, 59, 127, 128, 132, 133, 140, 142, 143, 144, 169, 187, 193, 298, 303, 304, 306, 307, 308, 313, 315, 416, 546
 Glyceryl esters, 187, 313
 Glycidol, 315, 316
 Glycocholic acid, 421
 Glycol, 128, 132, 169, 179, 184, 185, 312, 315, 316, 322
 ethylene, 184
 glyceryl stearate ("Glyceride"), 187
 monoaryl, 181
 monochlorhydrine, 184
 monoxylenyl glycol ethers, 184
 Goudron, 311, 425
 Goethite, 253
 Graefe's method, 543, 544
 Granite dust, 293, 294
 Graphite, 445, 464
 colloidal, 452, 464
 Gravel, 268, 428, 429, 432, 524
 Gravitation constant, 42
 Gravity, 141, 145, 270, 284, 285, 290, 293, 295, 304, 308, 344, 368, 375, 376, 386, 436, 536, 537
 chemical-centrifuge, 537
 differential, 223, 284, 291, 299, 375, 376, 385, 430
 of crudes, 221, 252, 263, 290, 537
 separation by, 322, 341, 342, 350, 356, 372, 378
 specific, 10, 11, 42, 48, 98, 106, 107, 141, 153, 159, 160, 222, 223, 249, 255, 263, 274, 289, 291, 293, 309, 373, 374, 377, 378, 423, 435, 475
 Gravity, specific, (Cont'd)
 492, 527, 535, 536, 540, 544, 545, 547, 550, 551, 552
 Greases, 221, 447
 cup, 447
 lubricating, 221, 447
 Green acids, 318
 soaps, 413
 Guaiacol, 47, 184, 185
 Gum, 23, 33, 78, 163, 178, 286, 409, 410, 413
 acacia, 31
 arabic, 15, 16, 29, 31, 32, 67, 75, 78, 167, 168, 174, 175, 178, 189
 damar, 29, 168, 177
 rosin, 168
 vegetable, 178
 wheat, 133
 Gypsum, 408
- ## H
- Halides, 527
 Halogen hydrides, 317
 hydrides, 190, 195, 316
 Halogenation, 324
 Heat, 160, 376, 480
 adsorbing solutions, 483
 exchanges, 242, 244, 252, 263, 282, 283, 285, 295, 330, 331, 332, 333, 358, 364, 369, 370, 381
 surfaces, 247, 249, 250, 269
 Heaters, 346
 cast-iron, 243
 coil-type boiler (open, closed), 234, 235, 236, 238
 direct-flame boiler, 234, 245, 268
 high-pressure steam, 234
 gas, 365
 low-pressure steam, 234
 pipe, 234, 237
 vertical, 245, 246
 Helmholtz' equation, 513
 Hematite, 294, 370
 Hemicellulose, 409
 Hemoglobin, 168
 Hendecenoic acid, 304, 306
 $\Delta\alpha$ -Heptadecene, 196
 Heptane, 68, 69
 Heptioic acid, 306
 aldehyde, 313
 Heptyl alcohol, 117, 128, 129
 Heptylic acid, 128, 129
 Heterocyclic amines, 190
 compounds, 179, 301
 Hexadecylene, 317
 Hexalin, 183, 187
 Hexamethylenetetramine alkylates, 183
 Hexamethylenetetramine arylates, 183
 Hexane, 431
 Hexanolsulfonic acid, 326
 Hexylene, 384
 Homogenization, 60, 98, 104, 153, 162, 163, 201, 203, 304, 413, 414, 426
 Homogenizers, 161, 162, 168, 195, 198, 201, 410, 414, 419
 Humic acid, 407, 409, 410, 413, 416, 417, 422, 426, 462
 Humus sol, 118
 Hydrated colloids, 30, 31, 32, 33, 34
 Hydrates, 104
 Hydration, 17, 26, 31, 32, 33, 34, 70, 86, 103, 136, 403, 425
 hypothesis, 30
 Hydrines, 319
 Hydroaromatics, 189, 190
 Hydrocarbons, 179, 189
 alcohol, 313
 emulsions, 75, 246
 oils, 45, 52, 93, 174, 238
 Hydrochloric acid, 9, 13, 41, 46, 47, 48, 51, 67, 75, 171, 274, 293, 325, 326, 327, 329, 333, 383, 408, 511, 527, 532, 542, 560
 Hydrochlorides, 449
 Hydrocinamic acid, 307, 308
 triisobutyl, 307

Hydrogen, 166, 167, 184, 186, 192, 296, 301, 303, 305, 307, 308, 311, 312, 317, 318, 462, 510, 518, 543, 548
 ion concentration, 11, 31, 32, 33, 43, 52, 61, 68, 70, 106, 147, 154, 176, 232, 274, 287, 288, 417, 418, 419, 421, 422, 423, 424, 433, 463, 504, 511, 512, 513, 532, 533, 542
 chloride, 326
 fluoride, 326
 number, 511
 peroxide, 330
 sulfate, 311
 sulfide, 275, 296, 329
 Hydrogenation, 185, 186, 189, 233, 290, 309, 463, 465
 products, 169, 320
 Hydrolyzing agents, 185, 317
 Hydrolysis, 8, 12, 25, 26, 27, 48, 59, 60, 70, 86, 87, 89, 90, 105, 107, 168, 173, 253, 287, 288, 300, 305, 311, 320, 323, 329, 405, 445, 526, 528, 533
 Hydrometer, 536, 537, 551, 552
 Hydrophilic colloids, 27, 30, 31, 33, 34, 69, 74, 104, 107, 148, 159, 167, 175, 176, 253, 271, 275, 297, 298, 414
 Hydrophobic colloids, 27, 31, 33, 69, 74, 107, 159, 167, 168, 176, 253, 271, 297
 Hydrophobization, 26
 Hydroquinone, 30
 Hydro-silicates, 384
 Hydroxides, 407
 Hydroxy alkylamides, 184
 anthracene, 314
 ethane, 312
 hendecenoic acid, 304
 monocyclo-sulfo aromatic group, 300
 oxyoctadeca-9, 11-dienoic acid, 300
 polycyclic compound, 314
 quinone method, 534
 stearic acid, 300
 Hydroxylamine, 195
 Hydroxylated acid, 314
 resin, 314
 Hydrotropic aliphatic compounds, 181
 Hyflo-supercel, 385
 Hygroscopic bodies, 159
 Hysteresis phenomenon in emulsions, 55

I

Illuminating oil, 328, 447
 Influence of electrolytes on emulsions, 64, 65, 66, 67, 69, 71
 on foams, 130, 131, 150
 Infusorial earth, 337
 Insulating oils, 459, 519
 Interface, liquid/gas, 175
 liquid/liquid, 22, 28, 68, 84, 90, 104, 163, 175
 Interfacial area, 86, 87, 88, 89, 93, 97, 99, 100, 155, 401
 layer, 12, 16, 19, 65, 66, 75, 76, 81, 84, 87, 88, 89, 90, 99, 101, 105, 136, 138, 140, 149, 150, 151
 tension, 3, 4, 5, 6, 7, 9, 10, 11, 12, 19, 20, 21, 30, 53, 60, 82, 84, 90, 92, 93, 103, 104, 105, 107, 126, 129, 134, 138, 150, 154, 165, 168, 170, 174, 187, 222, 270, 272, 302, 341, 400, 405, 409, 430, 431, 432, 445, 446, 447, 449, 450, 451, 458, 493, 494, 531
 tension measurements, 500-504
 viscosity, 15, 19, 22
 Inversion, critical point, 34, 37, 38, 62
 in emulsions, 60-72, 76, 98, 107, 108, 404
 of phases, 37, 60, 98, 107, 404
 point, 60, 62, 67, 107
 Iodides, 328, 403
 Iodine, 28, 30, 171, 172, 527, 532
 value, 458
 Iodobenzene, 43
 Ionic antagonism, 71
 atmosphere (Burton), 42, 43, 509
 Irish moss, 90, 168
 Iron, 65, 294, 295, 296, 337, 433, 455, 463, 549
 acetate, 127
 alum, 534

Iron, carbide, 549
 chloride, 286, 292, 293, 300, 329, 333, 430
 hydrosulfide, 29
 hydroxide (colloidal), 50, 173
 nitrate, 286
 ore, 294, 338
 oxides, 171, 176, 286, 329, 338, 383, 398, 408, 411
 pyrites, 81, 294
 salts, 176
 sulfate, 10, 56, 293, 326, 383, 403, 415, 423
 sulfide, 336, 383
 Isoamines, 180
 Isoamyl alcohol, 30, 69, 120, 128, 129, 130, 131, 132, 143, 234
 Isobutyl alcohol, 13, 69, 128, 129
 Isobutyric acid, 121
 Isocapillarity, 129
 Iso-colloids, 1
 Isoelectric point, 11, 33, 50, 51, 52, 271
 Isohexane, 10
 Isobexyl alcohol, 307
 Isomerization, 389
 Isomerism, dynamic, 380
 Isoparaffins, 446
 Isopropyl alcohol, 30, 193, 315, 320
 trimethylnaphthyl ammonium hydroxide, 193
 Isothionic acid, 191

K

Kambara earth, 384
 Kaolin, 19, 338, 427
 Kerosene, 6, 10, 15, 19, 21, 22, 28, 36, 38, 68, 74, 76, 77, 80, 85, 86, 87, 165, 173, 176, 272, 298, 302, 309, 310, 314, 321, 323, 330, 336, 340, 379, 382, 383, 384, 402, 464, 520, 540, 547
 Ketohydroxy-stearic acid, 300
 Ketones, 29, 169, 172, 179, 183, 184, 188, 189, 192, 193, 298, 301, 304, 319, 409, 428
 Kieselguhr, 30, 338, 370, 415

L

Lactic acid, 127, 128, 305
 Lacto-alcohols, 527
 Lactones, 193, 407, 526
 Lactose, 299
 Lampblack, 75, 80, 164, 167
 Lanolin, 29, 168, 174, 187
 Lanosyn, 187
 Lard, 447
 Latex, 410, 463, 546
 Lauric acid, 6, 172, 326
 Lauryl alcohol, 186, 188, 189, 194, 196, 312
 pyrimidine bisulfate, 185
 sulfuric acid ester, 186
 Lavender oil, 381
 Lead, 295, 433
 acetate, 186, 424
 arsenate, 29
 bromide, 424
 carbonate, 29, 412
 chloride, 19, 424
 chromate, 424
 glance, 134
 iodide, 424
 nitrate, 424
 oxide, 29, 428
 salts, 186
 sulfate, 29, 424
 sulfide, 428
 Lecithin, 54, 168, 174, 175, 318, 523
 soybean, 318
 vegetable, 318
 Lederer's formula, 68
 Lenard's fuzzing effect, 135
 Lepidolite, 294
 Lignic acid, 422
 Lignin, 170
 sulfonic acid, 313
 Lignite, 179, 409, 411, 540
 tar, 462
 Lime, 78, 79, 80, 147, 171, 176, 180, 190, 286, 293, 303, 325, 338, 408, 414, 417, 422, 426, 438, 463, 465, 528

- Limestone, 408, 433
 Linoleic acid, 185, 288, 301, 407, 450
 Linolenic acid, 169
 Linseed oil, 22, 40, 80, 147, 149, 172, 174, 232, 233, 295, 300, 305, 306, 322, 407, 409, 412, 447, 451, 521
 Liquefying agents, 411
 Lithium, 328
 oleate, 95, 96
 stearate, 67
 Lubricating oils, 5, 38, 55, 159, 183, 190, 274, 292, 309, 323, 324, 338, 349, 378, 380, 383, 384, 397, 415, 427, 445-466, 507, 520, 522, 525, 533
 adhesion, 455, 456
 capillarity, 447, 449, 450, 451
 compressibility, 456
 demulsification, 459, 460
 density, 447
 emulsibility of, 448, 461
 emulsification values, 460
 emulsions, 445, 461-466
 interfacial tension, 449
 molecular weight, 552
 oiliness, 447, 448, 453, 454
 polarity, 455, 456
 sludge formation, 457, 458
 stability, 458, 459
 tensile strength, 456, 457, 458
 viscosity, 447, 449
 wetting ability, 451, 452
 Lubrication, adsorption principles, 451, 452
 boundary, 447, 453, 455, 460, 462, 464
 degree of, 452
 efficiency or value, 452
 mechanism of, 449
 minimum, 453
 steam-turbine, 560
 viscous, 453, 455, 460, 464
 Lubricator, 277, 278, 279, 280, 285
 automatic sight-feed, 283, 284
 down-hole, 277, 278, 279
 force-feed, 280, 284
 high-pressure, 279
 inverted, 280
 low-pressure, 279
 Lyophilic colloids, 130, 131
 emulsions, 23
 foams, 130, 140, 149
 substances, 130
 Lyophobic foams, 131, 140, 149, 150
 sols, 131, 398
 substances, 130
 Lyotropic effect, 26
 series, 328, 329
- ## M
- Machine oil, 1, 451, 533, 553
 McKesson's method, 434
 Magnesite, 383
 Magnesium, 287, 295, 311, 328, 379, 383, 534
 carbonate, 249, 326, 408
 chloride, 249, 291, 212, 326, 328, 329, 333, 533
 hydroxide, 408
 oleate, 21, 29, 58, 61, 68, 69, 96, 298
 oxide, 370
 palmitate, 68, 69
 resinate, 297, 324
 salts, 171, 173, 192, 403, 405
 silicate, 418
 sulfate, 69, 249, 328, 430
 sulfonate, 189
 Magnetite, 295, 370
 Mahogany acids, 318
 Maleic acid, 302, 303, 304, 308, 319
 anhydride, 319
 Manganese oleate, 296, 324
 Maltose, 296
 Manganese oleate, 296, 324
 oxide, 353
 Mannite, 322
 Mannitol, 185
 Mannose, 175
 Marble, 294
 Marcusson's method, 434, 438
 Margarine oil, 523
 Mastic suspension, 18
 Masout, 397, 425, 461
 Menthol, 172
 Mercaptans, 465, 533
 Mercury, 166, 167, 449, 450, 456
 emulsions, 49, 166, 167
 foam, 166
 iodide, 81, 176
 sulfate, 449
 vapors, 404
 Metals, 125, 167, 295, 385, 449, 458, 460
 sulfides, 294
 oxides, 527
 Methane, 369
 Methyl alcohol, 20, 30, 180, 177, 196, 226, 233, 300, 322, 326
 amino sulfonic acids, 182
 cyclohexanol, 312
 dichlorostearate, 455
 ethyl ketone, 10, 30, 304
 hexalin, 69
 isobutyl ketone, 304
 naphthalene, 311
 orange, 72, 309, 532, 533
 propyl ketone, 128
 stearate, 455, 463
 sulfate, 180
 violet, 180
 Methylene blue, 433
 Mica, 137, 418
 Micro-Kjeldahl determinations, 233
 Microprojection equipment (Leitz), 483
 Microscopic examination of emulsions, 105, 220, 473-493
 dilution effect, 480
 disperse phase, 475
 heat effect, 480, 481
 electric effect, 480, 482
 formation, 475
 ingredients, 480
 type, 480
 Migration number, 519
 velocity, 44, 46, 515-519
 Mineral acids, 29
 matter, 383, 403
 oils, 1, 12, 23, 31, 38, 63, 90, 159, 170, 172, 176, 177, 178, 179, 183, 184, 185, 186, 187, 190, 193, 195, 197, 233, 250, 251, 267, 296, 309, 311, 318, 323, 327, 345, 355, 370, 381, 405, 412, 420, 426, 427, 428, 445, 447, 449, 450, 452, 454, 457, 459, 462, 463, 464, 521, 526, 531
 Miscibility test, 440
 Mohr's method, 533, 534
 Molasses, 197, 297, 451
 Molecular weight of petroleum and its products, 552
 Mono-ahetene, 318
 alkyl amide, 525
 amyl amino propane-2, 3-diol, 316
 aryl glycol ether, 181
 butyl- β -naphthalene sulfonic acid chloride, 310
 butyl-phthalate, 318
 chlorhydrate, 315
 chlorodiphenylene oxide, 455
 cyclic hydrocarbons, 527
 dodecyl ether, 308
 lauryl, 186
 methylsilyl glycerol, 186
 olein, 318
 oxyethyl-p-toluene sulfonamide, 319
 propylated naphthalene sulfonic acid, 326
 stearyl, 186
 glycerol, 185
 glycol, 185
 Montanic acid, 179
 Morphine, 449
 Motor oils, 459
 Myers' demulsibility test, 437
 Myricyl alcohol, 186
 Myristic acid, 6
 Myristyl alcohol, 188, 194

N

- Naphtha, 55, 196, 308, 381, 398, 447, 540, 543
 emulsions, 77, 81
 solvent, 300, 308, 402, 541
 Naphthalene, 45, 172, 182, 299, 308, 310, 311, 312, 314, 315, 317, 320, 323, 325, 417, 422, 462
 alkylated, 314
 alkylated-sulfonic acid, 304, 314, 315, 316, 319
 benzylamylbutyl, 169
 benzylbutyltetralin, 169
 benzylcyclohexyl, 169
 butylated-sulfonic acid, 314
 nitro, 185
 sulfonamide, 319
 sulfonic acid, 190, 195, 304, 310, 313, 314, 315, 316, 317, 319, 326
 sulfo-ricinoleate, 314
 Naphthenes, 185, 186, 328, 380, 526, 527, 550, 551
 Naphthenic acids, 6, 67, 77, 78, 154, 169, 177, 185, 187, 195, 237, 286, 288, 301, 309, 310, 311, 314, 318, 320, 323, 324, 327, 328, 379, 380, 382, 404, 405, 411, 413, 426, 459, 461, 525, 526, 527, 528, 532
 base crude oil, 310, 465
 hydrocarbons, 188, 297, 302, 303, 304, 379, 447, 463
 Naphthols, 29, 169, 172, 180, 299, 311, 317, 326
 Naphthyl acetic acid, 308
 amine, 148, 193
 butyrate, 300
 derivatives, 465
 propionate, 300
 Nastjukoff's test, 458
 Natural gas, 298, 303, 327, 337, 403, 428
 Neo-fuchsin, 449
 Neptune blue (R. G.), 439
 Nettel's method, 542
 Newtonian interference colors, 145, 483
 Nickel, 19, 295, 296, 433
 acetate, 296
 -chromium, 542
 formate, 296
 oxalate, 296
 oxide, 296
 salts, 176
 sulfate, 10
 tartrate, 296
 Nicotine, 185
 Nile blue dye, 532
 Nitrates, 228
 Nitration, 302
 Nitric acid, 127, 182, 327, 463
 Nitriles, 29, 169
 Nitrobenzene, 12, 29, 68, 69, 75, 128, 163, 176
 Nitro-compounds, 169, 193
 Nitrogen, 166, 167, 184, 191, 192, 311, 319, 369, 384, 404, 458
 bases, 303
 Nonylic acid, 71, 117, 120, 128, 129
 Noli (du) tensiometer, 90, 498
 Nujol, 22, 29, 38, 39, 40, 43, 61, 65, 67, 101, 168
 Nuttal's test, 458

O

- Octadeca-9, 11-dienoic acid, 300
 Octadecadiene acid, 305
 Octadecyl alcohol, 188
 chlorostearate, 455
 pyridinium bromide, 319
 Octadecylene, 317
 Octane oil, 58, 139, 484, 485, 487, 488, 489, 490, 533
 emulsions, 15, 58, 59, 88, 484, 485, 487, 488, 489, 490
 Octohydroanthracene, 310
 Octyl alcohol, 90, 92, 117, 128, 129
 aminoethyl-diethylbenzyl ammonium chloride, 180
 Oil-in-water emulsions, 9, 11, 15, 16, 21, 22, 26, 27, 29, 30, 33, 34, 35, 36, 37, 46, 50, 52, 53, 54, 58, 60, 61, 62, 65, 66, 67, 68, 69, 70, 71, 74, 76, 79, 80, 92, 93, 94, 95, 96, 97, 100, 101, 104, 106, 107, 153, 162, 167, 168, 170, 171, 173, 174, 175, 187, 197, 227, 233, 271, 273, 286, 292,

Oil-in-water emulsions, (Cont'd)

- 293, 294, 295, 296, 298, 327, 336, 337, 338, 339, 354, 373, 396, 403, 404, 405, 408, 412, 419, 423, 424, 425, 428, 445, 448, 480, 531, 532, 535
 Oil of cloves, 147, 149, 232
 Oleaginous material, 408
 Olefins, 188, 189, 191, 192, 317, 380, 384, 404, 446, 550
 Oleic acid, 6, 9, 30, 60, 66, 68, 89, 118, 136, 138, 140, 148, 162, 165, 166, 167, 169, 171, 172, 174, 175, 177, 179, 181, 190, 192, 195, 227, 228, 287, 288, 301, 303, 304, 308, 309, 311, 312, 314, 318, 404, 407, 409, 412, 414, 417, 418, 423, 446, 447, 451, 454, 533
 ethylanilide, 320
 hydrogen sulfate, 287
 propyl glycol esters, 190
 Olein, 303, 419, 447
 Oleosol, 397
 Oleophilic colloids, 27, 452
 Oleum, 180, 194, 407
 Oley alcohol, 102
 hydroxystearic acid, 287
 Olbanum (frankincense), 177
 Olive oil, 11, 12, 15, 22, 33, 36, 37, 38, 67, 73, 74, 80, 127, 174, 297, 308, 309, 480
 Optical absorption coefficient, 59, 486, 491, 492
 Optimum voltage in resolution of emulsions, 340
 Ores, 125, 132, 148
 Organic acids, 5, 275
 Orientation theory (Harkins-Langmuir), 90-102, 106, 108, 136, 138, 139, 140, 151
 Oriented wedge theory (Harkins), 87, 87, 94, 95, 96, 97, 98, 99
 Osmotic compressibility, 57
 pressure, 57
 Oxalates, 296
 Oxalic acid, 67, 303, 305, 319, 321
 anhydride, 319
 Oxalylamines, 182
 Oxidation, 233, 300, 305, 306, 309, 320, 321, 322, 369, 397, 404, 405, 408, 425, 426, 447, 458, 459, 461, 463, 520, 525, 526, 527
 number of oils, 558
 of oils, 521
 products, 194, 296, 303, 321, 324, 398, 407
 test, 558
 Oxides, 125, 296
 Oxy-acids, 190, 405
 alkylalkylamine, 316
 alkyl-di-alkylamine, 316
 amines, 180, 188
 benzene sulfo-acids, 318
 compounds, 320
 ethane sulfonate, 308
 ethyltoluenesulfonamide, 318
 fatty acid amides, 303
 fatty acids, 177, 181, 192, 303, 306, 319
 hendeceadiene acid, 305
 hendeceanoic acid, 305, 306
 lignin, 179
 octadecadiene acid, 305, 306
 ricinoleic acid amide, 303
 stearic acid, 309
 amide, 303
 stearin, 180
 sulfonic acid, 317
 Oxygen, 139, 166, 167, 300, 308, 329, 381, 382, 397, 405, 458, 459, 526, 558, 560
 Ozokerite, 302, 528, 552

P

- Packing effect, 108, 399
 of molecules, 93
 of spheres (Thomas), 35
 Palm oil, 194, 447
 Palmitic acid, 85, 169, 301, 450, 454
 Palmityl alcohol, 196
 phenol, 318
 p-amidophenol, 30
 cresol, 450
 dichlorobenzene, 185
 formaldehyde, 188, 296
 nitrophenol, 30

- Paraffin, 154, 159, 161, 173, 182, 187, 191, 194, 232, 233, 238, 324, 334, 384, 402, 419, 422, 463, 464, 465, 480, 531, 552
 base, 219, 280, 446, 465
 emulsions, 18, 23, 38, 80, 173, 175
 oil, 1, 6, 9, 10, 11, 19, 21, 24, 38, 45, 47, 49, 52, 54, 56, 66, 67, 74, 79, 89, 148, 172, 173, 175, 183, 280, 378, 451, 462, 520, 547, 549
 wax, 325, 326, 461, 526, 527, 552
 Paraffins, 55, 182, 183, 189, 190, 219, 327, 338, 384, 385, 397, 402, 405, 493, 527, 550, 552
 Paraldehyde, 128
 Peanut oil, 147, 149, 232, 447
 Peat, 413, 423
 Pectins, 175, 179, 190, 409
 Pendant drops, 503, 531
 Penetrometer, 436
 Pensky-Martens tester, 555, 556, 557
 Peptization, 27, 74, 131, 384
 Peptizing agents, 131, 140, 400, 401, 431
 Peptones, 84, 122, 124, 168
 Perchlorethylene, 318
 Peroxides, 521
 Perrin's law, 374, 437
 Petrol acid, 302, 303
 Petrolatum, 12
 Petrolene, 398
 Petroleum, 28, 30, 147, 149, 170, 172, 173, 175, 232, 239, 244, 246, 297, 299, 336, 347, 350, 379, 380, 412, 421, 451, 524, 525, 526, 528, 532, 540, 547, 549
 coke, 80
 crudes composition, 550
 distillates, 1, 10, 97, 187, 190, 320, 379, 380, 381, 383, 404, 411, 415
 emulsions, 39, 69, 75, 76, 79, 154, 168, 220, 221, 223, 233, 238, 250, 257, 258, 264, 266, 267, 272, 273, 274, 277, 283, 292, 293, 294, 295, 296, 297, 298, 299, 300, 301, 302, 303, 304, 305, 306, 307, 308, 309, 310, 311, 312, 313, 314, 315, 316, 317, 318, 320, 321, 322, 323, 324, 336, 337, 338, 345, 347, 348, 350, 351, 354, 355, 356, 366, 368, 370, 371, 372, 375, 475, 528, 542
 ether, 180, 410, 415, 535, 538
 maltha, 408
 oils, 6, 402, 427, 445, 475, 526, 527
 origin theories, 549, 550
 Ber's, 398
 Mendeleef's, 549
 Moissan's, 549
 organic, 550
 products, 325, 520, 547
 residues, 404, 411
 resins, 6, 273
 soaps, 275
 spirit, 78, 338, 384, 459, 553
 sulfonates, 286, 326
 sulfonic acid, 310, 314, 319
 tar, 168, 171, 265
 Pharmaceutical emulsions, 13, 21, 32
 Phase-volume relationship, 70
 Phenanthrene, 311, 325
 Phenanthryl capronate, 300
 derivatives, 465
 Phenetol, 43
 Phenol, 29, 30, 78, 169, 174, 177, 180, 181, 182, 183, 192, 196, 272, 274, 297, 298, 299, 301, 303, 311, 312, 314, 317, 318, 322, 326, 382, 413, 421, 428, 535, 536, 543
 aldehyde, 312, 315
 halogenated, 179
 hydrated, 178
 stearic acid, 300
 valeric acid, 308
 Phenolates, 382
 Phenolic acid, 532
 oil, 177
 Phenolphthalein, 533
 Phenones, 192
 Phenyl acetic acid, 307, 308
 alkylamines, 315
 amine, 428
 cresyl, 465
 formol (formolite), 381
 Phenyl, hexaline, 69
 mustard oil, 43
 oxide, 447
 valeric acid, 308
 Phosgene, 192
 Phosgenite, 294
 Phosphates, 531
 Phosphatidene, 318
 Phosphonium radical, 307
 Phosphoric acid, 171, 180, 189, 191, 195, 197, 317, 381, 410, 413
 Phosphorus, 321, 527
 bromide, 526
 chloride, 191, 195
 oxychloride, 191
 pentachloride, 191, 318, 322, 525
 pentoxide, 191
 Photomicrographs, 74, 375, 438
 of crude oil emulsions, 474, 476, 477, 478, 479, 481, 482
 Phthalic acid, 299, 303, 305, 319
 anhydride, 299, 302, 303, 306, 307, 308, 311, 313, 318, 319
 Phthalyl mono-olein, 304
 ricinoleic acid, 312
 Picric acid, 449
 Pimelic acid, 306
 Pine abietinic acid, 410
 Pinene, 384
 Pine oil, 233, 304, 309, 313, 327, 381
 Piperidine, 302, 318, 321
 Pitch, 172, 173, 177, 178, 407, 408, 410, 412, 414, 415, 424, 426, 429, 432, 451
 cottonseed oil, 422
 fatty acid, 416
 petroleum, 451
 stearin, 414, 422
 Plaster of Paris, 79, 176, 371
 Plateau's rule, 114, 116
 Poiseuille's law, 140
 Polar agents, 169, 286
 compounds, 29, 91, 178, 187, 286, 445, 455, 521, 544
 groups, 26, 65, 92, 93, 94, 95, 96, 126, 137, 140, 168, 169, 455, 456, 460
 molecules, 53, 85, 90, 91, 96, 97, 98, 101, 121, 286, 339, 455, 514, 521
 moment, 178
 Polarity, 12, 53, 85, 96, 175, 287, 493, 520
 of asphalts, 520
 lubricants, 455
 oxidized hydrocarbons, 520
 resins, 520
 unsaturated hydrocarbons, 520
 Polarized light, 483
 Polarization, 483
 effect, 483
 microscope, 480
 of the dielectric, 49, 340
 Poly-acrylic acid, 181
 hydric alcohols, 186, 195, 299, 306, 312
 hydroxy alkyl, 301
 hydroxy amine, 201
 keto acids, 305
 naphthenes, 526
 naphthenic acids, 527
 ricinoleic acid, 305
 ricinoleic acid amide, 182, 303
 arylide, 182
 saccharides, 409
 silicic acid, 416
 styrene, 191
 terpenes, 384
 valent alcohols, 29, 180, 181, 182, 303, 315, 316, 318
 vinyl acetate, 186
 vinyl alcohol, 186
 Polymerization, 186, 187, 188, 197, 309, 322, 377, 380, 381, 383, 384, 397, 404, 431, 447, 458, 462, 526
 Porphyry, 433
 Potash, 308, 405, 412, 438
 Potassium, 311, 328, 409
 carbonate, 9, 47, 181, 170, 383, 409, 412, 414, 462
 chaulmoograte, 97

Potassium, chloride, 9, 46, 47, 48, 50, 51, 292, 383.
430, 510

chromate, 414, 415, 533
citrate, 131
colophane, 127, 144
ferrocyanide, 46, 47
fluoride, 414
fluosilicate, 414
hydroxide, 172, 292, 308, 312, 383, 404, 407, 409,
410, 411, 413, 414, 417, 425, 441
iodide, 172
nitrate, 127, 144, 534
oleate, 66, 78, 95, 96, 297, 404, 410
palmitate, 57, 66, 69, 86, 97
permanganate, 534
rosinate, 422
salts, 403
stearate, 66, 86
sulfonaphthenate, 297
sulfonate, 189
tartrate, 383
thiocyanate, 534

Potential, 142, 356, 433
contact (thermodynamic), 101, 106, 510
critical, 9, 50, 51, 52, 106, 271
difference, 43, 44, 45, 46, 48, 49, 50, 51, 52, 106,
136, 271, 339, 340, 457, 510, 511, 512, 515
electrokinetic, 45, 46, 50, 53, 135, 509, 510, 513,
514, 515
electrostatic, 45
gradient, 340, 341, 350, 354, 509, 515
interfacial, 135, 509
mechanism by which set up, 509
streaming, 45, 85, 135, 513, 515

Pour point, 448

Pressure-volume relations, 226

Priming or puking of oil, 224, 225

Product integrals, 491

Production ability of petroleum drilling, 325, 326,
327

Propane, 397, 413, 428

Propionates, 27

Propionic acid, 41, 128, 129, 325

Propyl alcohol, 30, 128, 129, 169, 182, 303, 308,
322, 326

Propylene oxide, 301

Protective action, 107, 132, 222, 228
colloids, 16, 52, 78, 129, 130, 131, 132, 150, 170,
172, 188, 192, 197, 273, 297, 328, 398, 410,
411, 412, 414, 418, 427
number, 132

Proteins, 42, 73, 79, 136, 149, 168, 169, 170, 171,
174, 175, 193, 196, 232, 405, 407, 409, 416,
494, 515

Pumice, 205, 337, 438

Pumps, 154, 155, 158, 159, 346

belt-driven, 277
centrifugal, 344, 433
chemical proportioning, 277, 278
electrically driven, 277
high-pressure, 203
positive displacement, 344
ratchet-driven, 277
reciprocating steam, 344
rotary, 344

Pyhala's tests, 528

Pyrene, 2

Pyridine, 80, 176, 179, 180, 181, 303, 319, 320, 382,
431, 542, 546

Pyrimidine, 185

Pyrite, 295, 337, 433

Pyrophosphoric acid, 182

Pyrosulfuric acid, 312

Q

Quartz, 124, 125, 148, 166, 294, 295, 337, 370, 385,
515

Quillaja bark, 29

Quinine, 136

Quinoline acid, 73

Quinoline, 131, 179, 180, 320

R

Rape oil, 80, 320, 322, 447

Rayleigh's formula, 496

Red engine oil, 173

Red oil (2900), 10, 415

Re-centrifuging, 376, 386

Re-emulsification, 207, 254, 281, 294, 304, 335, 344,
355

Refining processes, 379-387, 533

with acids, 379, 380, 381, 383

adsorbents, 384, 385

alkalies, 379, 381, 382

electrolytes, 383

metals, 385

organic substances, 383

oxidation, 383

salts, 382

Refractive index, 475, 520, 527, 550, 552

of minerals, 480

oils, 480, 553

solid paraffins, 552

Refractivity (specific), 527

Refractometers, 552

Removal law (Michaelis, Rona), 132

Resinates, 168

Resins, 28, 30, 76, 77, 148, 172, 174, 175, 176, 177,
179, 185, 190, 297, 301, 309, 326, 376, 378, 379,
381, 402, 403, 405, 407, 410, 411, 413, 415, 417,
420, 422, 425, 427, 429, 432, 459, 464, 520,
540

acids, 177, 193, 303, 323, 409, 410

Resorcinol, 29, 169

Ricinoleate, 288

Ricinoleic acid, 187, 300, 303, 304, 305, 306, 307.

308, 312, 313

amide, 303

ester, 180

Ricinoleyl, 301, 318

phthalate, 301, 313

Ring method, 53, 497

Rock oils, 549

Rolly oil, 220, 297

Rosenthal's reaction, 527

Rosin, 29, 232, 404, 413, 422

acid, 301, 415

oil, 404

Rubidium, 328

oleate, 95, 96

Rubber, 432, 456, 463

latex emulsions, 54, 418

vulcanized, 403

S

Saccharides, 411

Salicylic acid, 181, 449

Salol, 172

Salting-out, 6, 26, 28, 197, 328, 329, 379, 380, 403

Salt tests, calcium and magnesium, 534

chlorides, 533, 534, 535

sulfates, 534

Samplers, bombs, 469, 470

bottle, 468, 469

copper tube, 469, 470

piston-controlled, 472, 473

pressure-controlled, 469, 472, 473

sudden admission, 472, 473

thief, 470, 471

trap-bailer, 469

Sampling of emulsions, 468-474

bottom-hole, 471

bottom-hole pressure, 471, 472, 473

Sand, 32, 148, 154, 155, 220, 221, 225, 263, 292, 293,
294, 297, 303, 330, 370, 371, 402, 404, 411, 420,
421, 429, 430, 524, 528, 529, 547

Saponification, 170, 177, 182, 186, 189, 197, 298,
301, 314, 320, 382, 407, 408, 412, 414, 415, 417,
533

Saponifying agents, 182, 414, 428

Saponin, 15, 22, 29, 72, 73, 74, 78, 84, 90, 118, 121,
122, 124, 127, 130, 132, 133, 136, 144, 146, 148,
168, 174, 175, 297, 410, 411

Savonade (Hexalin soap), 177

Scarlet red dye, 532

Schacic acid, 304, 306

- Sebazinic acid, 303
 Self-cooling effect, 147, 230, 231
 Separators, 230, 249, 255, 256, 258, 285
 capillary, 267
 centrifugal, 372, 376, 377, 378
 de Laval, 372, 377
 electro-centrifugal, 378
 gas, 262, 263, 281, 330, 364, 365
 gun-barrel, 239
 high pressure, 267
 magnetic, 372
 Serpentine, 433
 Settling test, 436, 437
 Shale oil, 415, 447, 545
 distillates, 187
 Shark-liver oil, 191
 Sieve test, 440
 Silica, 52, 66, 79, 81, 176, 286, 384, 385, 408
 gel, 383, 385, 418
 Silicates, 183, 295, 411, 422
 Silicic acid, 416
 sol, 78
 Silicon oxide, 176, 408, 410
 oxide gel, 433
 Silver, 433, 517
 chromate, 533
 nitrate, 424, 518, 533, 534
 salt, 528
 sulfate, 424
 Size frequency analysis, 18, 107, 299, 483, 492
 Slate, 338
 flour, 427
 Sludge, 16, 147, 172, 187, 188, 190, 197, 220, 232,
 272, 291, 292, 298, 303, 308, 310, 323, 325,
 335, 350, 371, 375, 404, 408, 410, 415, 425, 458,
 463, 465, 560
 Sludging phenomenon, 366, 430
 Smectic state of soaps, 25
 Soaps, 2, 7, 8, 13, 25, 26, 29, 30, 34, 36, 37, 54,
 62, 66, 67, 70, 78, 85, 86, 87, 92, 93, 95, 100,
 107, 115, 124, 127, 132, 133, 136, 141, 142, 145,
 146, 148, 159, 161, 165, 166, 167, 168, 170, 171,
 172, 174, 177, 178, 180, 181, 183, 184, 187, 189,
 193, 195, 197, 210, 221, 228, 271, 273, 274, 275,
 286, 287, 292, 298, 302, 303, 323, 326, 376, 379,
 382, 399, 401, 405, 406, 407, 408, 409, 410, 413,
 414, 415, 417, 418, 420, 421, 422, 423, 424, 425,
 426, 428, 430, 432, 434, 437, 445, 454, 459, 462,
 465, 462, 494, 528, 531, 533, 540
 acid, 159
 alkali, 26, 57, 70, 97, 406, 428, 464
 alkali metal, 96
 alkaline earths, 29, 97, 273, 288
 aluminum, 29, 95, 97
 ammonium, 159, 298
 ammonium resin, 423
 calcium, 71, 273, 371
 cesium, 57, 58, 96, 97, 437, 463
 fatty acid, 382, 405, 535
 green acid, 413
 heavy-metal, 95
 iron, 29
 magnesium, 371
 Marseille, 127, 144
 naphtha, 376
 naphthenic acid, 28, 76, 77, 178, 298, 303, 461,
 528
 oleic acid, 85
 olein, 165
 palmitic, 85
 paraffin, 160
 potassium, 25, 29, 57, 58, 78, 94, 97, 185, 187,
 410, 417, 463
 resin, 144, 165, 167, 174, 177, 196, 410, 413, 414,
 417, 421
 ricinoleic acid, 165
 rosin, 404, 415, 422
 sodium, 25, 26, 57, 58, 67, 71, 94, 96, 171, 298,
 417
 stearic, 85
 sulfo, 298
 sulfonic, 187
 zinc, 29, 95
 Soda (caustic), 88, 72, 170, 174, 188, 189, 275, 286,
 292, 295, 308, 330, 405, 528, 531, 533, 549
 Sodium, 6, 293, 308, 311, 328, 379, 543, 548, 549
 acetate, 172, 292, 329, 330, 463
 aluminate, 433
 bicarbonate, 286
 caproate, 8
 caprylate, 6, 8, 27
 carbonate, 7, 127, 144, 175, 249, 291, 292, 324,
 383, 408, 409, 412, 426, 427, 433, 462
 cetyl sulfate, 64, 65, 102
 cetyl sulfonate, 68
 chloride, 6, 67, 71, 165, 171, 172, 249, 286, 292,
 297, 303, 310, 323, 326, 333, 403, 408, 413, 416,
 422, 430, 461, 534, 544
 cholate, 118
 chromate, 415, 417
 cresolate, 433
 dicesylphosphate, 179
 ditolylphosphate, 179
 ethyl oleate, 327
 ferrocyanide, 299
 glycerin sulfonate, 318
 glycocholate, 72, 90, 122, 449
 hydroxide, 6, 46, 59, 60, 63, 66, 67, 80, 86, 89,
 90, 165, 170, 172, 173, 174, 176, 177, 182, 183,
 188, 197, 291, 292, 293, 303, 308, 312, 317,
 323, 324, 329, 381, 383, 404, 407, 408, 409, 411,
 413, 414, 415, 417, 418, 420, 422, 423, 428, 429,
 430, 433, 461, 463, 511, 527, 542
 iodide, 28
 isoathionate, 318
 isopropyl- β -naphthyl sulfate, 295
 laurate, 8, 27
 lauryl sulfate, 12
 lysabonate, 13
 naphthenate, 528
 nitrate, 80, 176
 nitrite, 463
 oleate, 6, 8, 15, 18, 21, 22, 23, 26, 29, 30, 36,
 38, 39, 48, 54, 58, 59, 60, 61, 62, 63, 64, 66,
 67, 68, 69, 72, 77, 86, 88, 89, 90, 95, 96,
 97, 98, 102, 124, 163, 166, 287, 297, 298, 440,
 484, 485, 487, 488, 489, 490, 491, 531, 533
 ortho-vanadate, 300
 oxalate, 415
 oxvethansulfonate, 308
 palmitate, 7, 27, 57, 66, 97
 perborate, 330
 peroxide, 330
 phosphate, 166, 299, 408, 409, 412, 413, 414, 415,
 417, 421, 423
 plumbate, 433
 potassium alloy, 548
 protalbinat, 13
 resinate, 29, 177, 297, 298, 378
 salicylate, 184, 185
 snits, 313, 409
 silicate, 166, 297, 298, 407, 413, 417
 stearate, 7, 27, 66, 73, 531
 sulfate, 67, 190, 249, 275, 286, 292, 297, 305, 328,
 403, 413, 433, 533
 sulfide, 415
 sulfite, 408, 415, 417, 420, 528
 sulfobenzylricinoleate, 311
 sulfonate, 189, 311
 tetraborate, 463
 thiosulfate, 415
 zincate, 433
 Softening point, 435, 439
 Solar oils (Baku), 382
 distillate, 10
 Solid/liquid interface, 7, 506
 Solids, 7, 10, 19, 20, 32, 33, 55, 62, 66, 73, 74, 75,
 78, 79, 80, 81, 83, 84, 103, 104, 125, 126, 130,
 133, 134, 136, 138, 139, 148, 150, 155, 205, 254,
 294, 370, 406, 413, 453, 455, 464, 533, 534, 535,
 551
 Solubility, 7, 11, 12, 14, 61, 70, 78, 91, 117, 118,
 120, 121, 127, 149, 187, 270, 272, 274, 275, 287,
 328, 400, 406, 431, 435, 536, 541, 548, 549
 colloidal and molecular, 1, 2, 24, 25, 96, 103, 104,
 119, 123, 127, 130, 133, 149, 167
 in emulsions, 23-31
 foams, 121, 122, 123, 124, 125

- Solubility, of water in
 benzene, 547, 548
 gasoline, 547, 548
 hydrocarbons, 547
 Solvated colloids, 29
 Solvation, 26
 Solvents, 96, 121, 134, 178, 179, 182, 183, 184, 188,
 190, 191, 192, 286, 296, 297, 308, 312, 315,
 381, 382, 385, 386, 401, 402, 406, 411, 412, 413,
 420, 422, 427, 428, 429, 534, 535, 538, 539,
 542, 545, 546
 Soot, 80, 176
 Sorbite, 322
 Sorbitol, 185
 Soybean flour, 182, 413
 oil, 322, 409, 447, 462
 Sperm oil, 410
 Spermacetic oil, 318
 Spindle oil, 76, 77, 197
 Spreading, 115, 120, 121, 123, 124, 126, 128, 137,
 139, 228, 419, 521, 532
 ability, 104, 126
 coefficient, 4, 83, 104, 120, 126, 432
 tension measurements, 504
 Stability, 136, 431, 458, 465
 of emulsions, 9, 11, 12, 13, 14, 16, 17, 22, 32, 33,
 38, 39, 42, 50, 51, 52, 53, 56, 58, 59, 68, 72,
 74, 88, 93, 96, 97, 98, 100, 101, 105, 106, 107,
 153, 166, 168, 172, 175, 178, 222, 270, 271, 273,
 274, 286, 322, 328, 336, 364, 375, 376, 378, 400,
 401, 405, 406, 410, 411, 413, 415, 416, 417, 419,
 423, 424, 425, 429, 432, 433, 436, 462, 480, 484,
 485, 486, 487, 488, 489, 490, 491, 523, 530, 531
 measurement (Berkman's method), 53, 59, 486
 of foams, 124, 128, 129, 130, 131, 132, 133, 134,
 135, 136, 137, 138, 139, 140
 Stabilization, 3, 13, 15, 23, 24, 30, 41, 48, 50, 65,
 68, 74, 75, 79, 81, 82, 96, 97, 98, 103, 106, 107,
 129, 132, 133, 134, 136, 150, 166, 170, 173, 174,
 221, 271, 277, 339, 376, 405, 407, 408, 421, 422,
 425, 426, 433, 531, 545
 Stabilizing agents, 22, 52, 61, 75, 78, 97, 100, 101,
 105, 106, 125, 134, 137, 138, 139, 148, 150, 151,
 166, 170, 171, 179, 182, 186, 188, 221, 286, 288,
 295, 302, 303, 401, 406, 410, 413, 414, 417, 418,
 420, 426, 428, 429, 528
 Standard silocel, 385
 Stanolax (heavy paraffin oil), 15, 58, 59, 68, 88,
 480, 491, 533
 emulsions, 15, 491
 Stanolind, 40, 43
 Starches, 20, 29, 33, 78, 103, 168, 172, 174, 286, 297,
 298, 301, 326, 376, 406, 409, 411, 412, 413, 423
 Stearate foam, 232
 sol, 232
 Stearic acid, 30, 169, 180, 183, 184, 227, 233, 301,
 303, 314, 419, 450, 455, 543
 amide of, 178
 chloride of, 192
 oxyethylamide sulfuric acid ester, 183
 Stearins, 176
 Stearolactone, 297, 311
 Stearyl alcohol, 318
 Stern's equation, 514
 Stokes' equation, 18, 43, 373, 374, 430
 Stretching phenomena of liquids, 227
 Strontium, 328
 oleate, 298
 Styrene, 169, 181
 Suberic acid, 806
 Succinic acid, 302, 303, 304
 anhydride, 186
 Sucrose, 19, 28, 29, 175
 Sudan III dye, 532
 Sugar, 20, 28, 117, 128, 169, 178
 Sulfamides, 184
 Sulfates, 125, 249, 328
 Sulfides, 125, 533
 Sulfite, 177, 313, 426
 Sulfo-acetic acid, 181, 194
 acid, 295, 305, 310, 311, 313, 318, 380, 381, 382,
 411
 amino acids, 193, 194
 aryl esters, 311
 carboxylic amide, 320
 Sulfo-chlorides, 184, 318
 compounds, 303, 319, 533
 cyanide, 328
 fatty acid, 303, 320, 321
 hendecenoic acid, 311
 octadecyl toluene monosulfonic acid, 195
 oleic acid, 309, 311
 oxanthracene resinates, 314
 palmitic acid, 182
 succinic acid, 313
 Sulfonation, 174, 180, 181, 182, 187, 188, 189, 190,
 191, 192, 193, 194, 196, 299, 309, 310, 311, 314,
 315, 317, 318, 320, 324, 380, 397, 407, 546
 Sulfonated alkyl naphthalenes, 178
 amines, 315
 anhydride, 312
 aromatic compounds, 314, 404
 benzyl butyl naphthalene, 169
 carbazol, 192
 castor oil, 309, 313, 326
 fats, 181, 189
 fatty acids, 181, 189, 302, 313, 405, 445
 mineral oils, 314
 oils, 167, 168, 172, 181, 187, 188, 189, 190, 193,
 195, 233, 302, 308, 309, 327, 404, 426, 459
 oleic acid, 305, 326
 oleophenone, 192
 palmitic acid, 29
 phenolformaldehyde products, 190
 phenol oxymethylene, 312
 phenylbutyl naphthalene, 169
 polycyclic aromatic compounds, 314
 products, 185, 188, 189, 192, 193, 194, 233, 288,
 301, 309, 313, 317, 318, 320, 327, 406, 408
 soaps, 308
 stearic acid, 29
 Sulfonating agents, 184, 188, 190, 191, 193, 312,
 316, 317, 415
 Sulfonic acid, 28, 29, 168, 169, 172, 174, 181, 182,
 183, 185, 187, 188, 189, 190, 191, 192, 193,
 195, 196, 297, 299, 309, 310, 311, 312, 315,
 318, 319, 320, 327, 328, 411, 415, 419, 461, 463
 amino oxyalkyl-oxyaryl, 192
 imino oxyalkyl-oxyaryl, 192
 oleo, 287
 Sulfur, 321, 336, 379, 381, 384, 385, 427, 459, 463
 compounds, 384, 461
 content of oil, 560
 determination in oil, 559, 560
 dioxide, 226, 296, 528
 flowers of, 464
 trioxide, 77, 187, 192, 195, 313, 323
 Sulfuric acid, 28, 75, 127, 163, 172, 180, 183, 184,
 186, 187, 188, 189, 190, 192, 193, 194, 195,
 197, 225, 274, 286, 291, 297, 298, 299, 301,
 303, 305, 307, 308, 309, 312, 313, 315, 317, 318,
 320, 321, 323, 327, 340, 379, 380, 382, 383,
 385, 404, 408, 410, 415, 434, 461, 463, 483,
 533, 534, 545, 546
 Sulfurization, 190, 305, 318, 320, 321
 Sulfuryl chloride, 822
 Sunflower oil, 175
 Superheated steam (cooking in vats), 223
 Superheating phenomenon, 147, 224, 225, 226, 227,
 228, 230, 231
 Superoxides, 458
 Supersaturation of gases, 227
 Surface active substances, 117, 120, 122, 123, 129,
 130, 132, 134, 135, 149, 306, 307
 activity, 9, 118, 119, 120, 123, 124, 127, 129, 133,
 149
 colors, 483
 polarization phenomenon in emulsions (S.
 Berkman), 480, 483
 refraction, 483
 tension, 400, 401, 431, 449, 450, 451, 458, 459, 462,
 493, 494, 500, 535
 in emulsions, 2, 3, 6, 7, 8, 9, 10, 11, 12, 13,
 14, 16, 22, 28, 33, 51, 53, 60, 61, 71, 72, 73,
 76, 77, 81, 103, 105, 154, 168, 172, 175, 266,
 272, 275, 296, 308, 337, 401, 405, 431, 470, 532
 in foams, 114, 115, 116, 117, 118, 121, 122, 123,
 124, 129, 131, 134, 137, 140, 142, 143, 145, 146,
 147, 148, 149, 151, 232, 233
 measurements, 494-500

Surface tension, waves (ripples) method, 497
 Sweating phenomenon, 433
 Sweet almond, 15
 Switch oils, 447, 457, 520
 Szegvary's diaphragm, 25
 Szyskowski's equation, 120

T

Tallow, 182, 187, 197, 233, 447, 463
 oils, 410, 447
 Tank-bottom emulsions, 156, 220, 247, 248, 270, 282, 289
 gun barrel, 239, 240, 241, 255, 260, 280, 283, 332
 Hay, 260
 open, 223
 settling, 244, 251, 252, 255, 258, 260, 265, 278, 280, 284, 285, 330, 359, 372
 screening, 275
 storage, 245, 295, 325, 344
 wash, 252
 Tannic acid, 174, 415
 Tannin, 75, 174, 409
 Tars, 12, 170, 171, 172, 176, 177, 178, 180, 190, 197, 239, 246, 249, 250, 257, 267, 301, 322, 323, 328, 349, 356, 378, 379, 400, 404, 405, 406, 407, 408, 409, 410, 411
 beech-wood, 184
 mineral, 461
 oil, 185, 187, 325, 382, 406, 411, 412, 415, 417, 420, 423, 424, 425, 432, 452
 oil emulsions, 36, 172, 177, 188, 239, 256, 301, 337, 422, 426, 427, 429, 540, 543, 545
 residues, 177, 230
 Tartaric acid, 27, 303, 304
 Tartrates, 296
 Taurocholic acid, 421
 oil, 418, 420
 Tensile strength test, 521, 522
 Terpenic hydrocarbons, 313, 381, 382
 Terpeneol, 190
 Tesla coil, 166
 Tetra-chlorethane, 186, 296
 chloroethylene, 296
 chlorostearic acid chloride, 183
 decyl alcohol, 194
 dodecyl alcohol, 194
 hydronaphthalene, 192
 ethylene pentamine, 317
 sulfonic acids, 179
 iodofluorescein
 isobutylhydrocinammic acid, 308
 propyl benzene sulfonic acid, 308
 Tetralin, 66, 187, 302, 326
 Theory of equi-partition of energy, 99
 Thionyl chloride, 322
 Thioisulfonic acid, 193
 Thiourea, 174
 Thixotropy, 400
 Thorium, 65
 chloride, 46, 50
 nitrate, 47, 48, 51
 Thymol, 172
 Tin, 295, 433
 chloride, 424
 iodide, 424
 sulfate, 424
 phosphate, 424
 salts, 186
 Tintometer (Lovibond), 553
 Titanium chloride, 424
 fluoride, 424
 oxide, 370
 Titration voltmeter, 517, 518
 Toluene, 11, 12, 38, 41, 54, 67, 69, 81, 137, 175, 176, 190, 192, 195, 308, 309, 311, 314, 415, 540, 541
 disulfonic acid, 326
 Toluidine, 128, 129, 319, 326
 Topping plant for breaking emulsions, 223, 248, 371
 Tragacanth, 15, 31, 32, 90, 168, 174, 175
 Transformer oil, 24, 170, 197, 447, 457, 519, 520, 521

Transition to the unstable state (foams), 142-147
 Traps, squeeze, 262
 water, 260
 Traube's rule, 119, 135, 494
 stalagmometer, 449
 Tret-o-lite, 12, 298, 538
 Tri-bromhydrine, 43
 chloroethylene, 185, 318
 chloronaphthalene, 455
 chlorophenol, 455
 ethanol, 311
 ethanolamine, 90, 174, 180, 181, 184, 185, 195, 300, 304, 305, 314, 317, 318, 321
 ethanolamine chloride, 184
 ethanolamine oleate, 22, 415, 417
 ethyl ammonium, 21
 ethylbenzyl ammonium chloride, 308
 ethylenetriamine, 317
 glycerides, 306
 isobutylphenyl acetic acid chloride, 308
 propyl naphthalene sulfonic acid, 314, 315
 methyl naphthyl ammonium methyl sulfate, 193
 methyl octyl phosphonium propyl sulfate, 307
 olein, 539
 oxyethylamine stearate, 169
 propylbenzene sulfonic acid, 308
 ricinolein, 305
 dioxalyl triricinolein, 305
 Turbine oils, 197, 459
 Turkey-red oil, 172, 174, 188, 190, 288, 302
 Turpentine, 19, 127, 131, 143, 144, 174, 176, 381, 409, 422, 464, 539
 resins, 409
 Twitchell reagents, 182
 Type of emulsion (determination, drop-dilution method, 531, 532
 indicator method, 532

U

Ultrafiltration, 403
 Ultramicros, 1, 271, 373, 492
 Ultramicroscope, 1, 403, 475, 492
 Ultramicroscopic investigation, of asphalt bitumen, 400
 of emulsions, 486, 492
 of particles, 1, 27, 28, 492
 Ultrasonic dispersion, 167
 waves, 166, 167, 197
 Ultraviolet rays, 372, 475
 Union colorimeter, 553, 554
 Urea, 174, 301
 Urethanes, 184, 192, 494

V

Valerates, 27
 Valeric acid, 128, 129, 454
 Valves, 158
 check, 265
 float, 263
 gate, 260
 pressure, 266
 spring-loaded relief, 369
 water-discharge, 262
 Valvoline oils, 446
 Van der Waals' equation, 227
 theory, 57
 Vanillin, 527
 Vaseline (petroleum jelly), 221, 378, 461, 520
 emulsions, 49, 50
 -like residue, 180
 Vegetable oils, 31, 78, 147, 149, 177, 178, 184, 186, 188, 196, 232, 298, 309, 409, 447, 449, 454, 463, 533
 emulsions, 31
 Vibrating drop method, 497
 jets method, 496
 Viscometers, 400, 509
 Engler, 448, 507, 508
 Hoppler, 508
 Michell, 448
 Ostwald, 448, 508
 Redwood, 448, 507, 508

Vismeters, Saybolt-Universal, 448, 506, 507, 508
 Steiner, 508
 Ubbelohde, 508
 Vogel-Ossag, 448, 508
 Viscosity, 13, 15, 16, 18, 19, 20, 21, 22, 23, 65, 89,
 103, 104, 105, 107, 117, 120, 121, 129, 130, 133,
 140, 141, 143, 149, 150, 153, 168, 171, 221,
 222, 223, 264, 265, 270, 273, 274, 286, 289, 291,
 296, 299, 309, 335, 339, 353, 369, 371, 376, 377,
 380, 399, 400, 419, 425, 426, 430, 433, 436, 448,
 449, 453, 457, 459, 461, 462, 463, 464, 470, 507,
 515, 525, 532, 540, 543
 coefficient 18, 141
 Einstein's equation, 17, 18
 factor in emulsification, 19, 20, 21, 23, 28
 stability, 22, 23
 Halseck's equation, 18
 internal and superficial, 15, 18, 19, 20, 22, 23,
 124, 143, 144, 146, 150
 kinematic, 508
 limiting, 23
 measurements, 507-509
 number, 417
 quasi, 400
 Volatility, 142, 146, 150, 160, 251
 Volhard's method, 533, 534
 Volume relation, 34-40

W

Water determination, 537-550
 in coal tar, 541
 gasoline and benzene, 546
 greases, 541
 molasses, 539
 oils, 540
 tars, 540, 545
 transformer oil, 549
 methods, acetylene, 544
 centrifuge, 538, 545
 distillation, 538, 539, 540, 541, 545
 freezing, 546, 547
 latex-copper sulfate, 546
 Water-gas emulsions, 238
 tar, 325, 369
 Water glass, 295, 298, 385, 410, 411, 420, 426
 Water-in-oil emulsions, 10, 21, 27, 29, 30, 33, 34,
 35, 36, 38, 39, 47, 49, 50, 52, 58, 60, 61, 62,
 63, 64, 65, 66, 67, 68, 69, 70, 74, 79, 80, 92,
 93, 94, 95, 96, 98, 100, 107, 153, 162, 166,
 167, 168, 170, 174, 185, 186, 187, 219, 220, 221,
 251, 272, 275, 286, 292, 293, 295, 296, 297, 299,
 300, 301, 305, 306, 309, 311, 312, 313, 314, 315,
 320, 321, 323, 324, 326, 334, 339, 342, 348, 349,
 354, 376, 378, 396, 404, 405, 413, 419, 423, 424,
 425, 448, 460, 463, 531, 532, 536
 knock-out system, 260
 softeners, 280, 298, 302
 Wax, 29, 169, 174, 175, 176, 179, 182, 184, 185, 187,
 188, 189, 190, 196, 199, 220, 221, 317, 411, 412,
 461, 538
 bees, 317
 candleilla, 463
 carnauba, 317, 318
 flax, 317
 montan, 29, 178, 179, 190, 414, 418
 wool, 317
 Well-gauging, open-type meter, 473
 vapor-tight meter, 473

Wells, 325, 532
 flowing, 154, 156, 157
 gas-lift, 154, 156, 157, 285, 289
 pumping, 154
 swabbing, 157
 Westrumite, 418
 Wetted septum (Cottrell), 336, 341
 Wetting, 19, 79, 80, 81, 83, 104, 107, 124, 125, 128,
 138, 139, 148, 150, 165, 168, 176, 181, 226,
 287, 294, 295, 297, 336, 337, 351, 370, 426, 449,
 451, 504, 552
 ability, 12, 14, 61, 71, 74, 78, 81, 85, 154, 192, 194,
 451, 452
 agents, 326
 heats of, 451, 452, 504
 hysteretic of, 505
 pressure, 452, 453
 selective, 82, 258
 tension, 505, 506, 507
 tension measurement, 504, 505
 velocity, 506
 Whale oil, 147, 177, 180, 197, 232, 407, 412, 447,
 521, 523
 White oils, 323, 410, 459
 Wick lamp, 560
 Wilkinite, 422
 Woelfin's chart (gravity of oil), 536
 Wood, 179, 294, 417, 423
 oil, 40
 tar, 546
 Wool, 205
 fat, 410, 412, 414
 grease, 45, 178, 187
 Work of adhesion, 4, 91, 120, 126
 cohesion, 4, 91, 120
 extension, 3

X

Xanthogenate, 148
 X-rays, 372, 455
 Xylene, 30, 41, 43, 61, 67, 184, 192, 226, 232, 308,
 309, 311, 326, 386, 411, 434, 535, 539, 540, 541,
 542, 543
 sulfonamide, 319
 Xylenols, 184, 185, 274, 322
 Xylidine, 148

Y

Yeast, 80
 Young's gravitometer, 551, 552
 theory, 115

Z

Zeolites, 294
 Zinc, 81, 269, 295, 433, 455
 blende, 124, 138
 bromide, 424
 chloride, 29, 196, 317, 318, 424
 cyanide, 424
 dust, 80
 fluoride, 424
 iodide, 424
 nitrate, 424
 oxychloride, 29
 oxide, 171
 phosphate, 424
 sulfate, 10, 408, 424
 Zirconium nitrate, 424

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